

GA 1751



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of: Bednorz et al.

Docket No.: YO987-074BY

Serial No.: 08/303,561

Group Art Unit: 1751

Filed: 09/09/94

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

Assistant Commissioner for Patents
Washington, D.C. 20231

CERTIFICATE OF MAILING UNDER 37 CFR 1.8 (a)

I hereby certify that the attached correspondence comprising:

1. Appellant's Reply To The Examiner's Answer
(With Attachments A, B and C) (3 sets)
2. Acknowledgment Card

is being deposited with the United States Postal Service as first class mail in an
envelope addressed to:

**Assistant Commissioner for Patents
Washington, D.C. 20231.**

on July 17, 2000

Jennifer A. Smith

(Type or printed name of person mailing paper or fee)

Jennifer A. Smith
(Signature of person mailing paper or fee)

BEST AVAILABLE COPY

RECEIVED
JUL 21 2000

RECEIVED
JUL 21 2000

TC 1700 MAIL ROOM
TC 1700 MAIL ROOM

BEFORE THE BOARD OF PATENT APPEALS

AND INTERFERENCES



Paper No. 91

Application Number: 08/303,561

Filing Date: September 09, 1994

Applicants: Johannes G. Bednorz et al.

Daniel P. Morris
For Appellant

APPELLANT'S REPLY TO THE EXAMINER'S ANSWER

REQUEST FOR REMAND

Appellants request remand of the present application to the examiner since the examiner introduced a new ground for rejection in the examiner's answer to the appellants' brief.

In the answer at section (10) "Grounds of Rejection" the examiner states:

The following ground(s) of rejection are applicable to the appealed claims:

Application 08/303,561

RECEIVED
JUL 21 2000
TC 1700 MAIL ROOM

RECEIVED
NOV 24 2000
TC 1700 MAIL ROOM

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

The present specification is deemed to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element or Group III B element.

Note that the above 112, first paragraph, rejection has been modified in scope from the Final Office Action. Upon careful consideration of the evidence as a whole, including the specification teachings and examples, and applicant's affidavits and remarks, **the examiner has determined that the instant specification is enabled for compositions comprising a transition metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element (as opposed to only compositions comprising $\text{BaLa}_{1-x}\text{Cu}_x\text{O}_y$ as stated in the Final Office action).**

Applicant has provided guidance throughout the instant specification that various transition metal oxides (such as copper oxide) containing an alkaline earth element and a rare earth or

Group IIIB element result in superconductive compounds which may in turn be utilized in the instantly claimed methods.

Appellants disagree that they have only enabled compositions containing an alkaline earth element and a rare earth or Group IIIB element to result in superconductive compounds which may in turn be utilized in the instantly claimed methods. This new ground for rejection necessitates the introduction of new evidence to show why the examiners statement is incorrect. There are numerous examples of high Tc superconductors made using the general principals of ceramic science as taught by appellants that existed prior to appellants' earliest filing date. The affidavit of Duncombe submitted by appellants specifically recites some of the compounds reported on in the several hundred pages included from his lab note books which include: $Y, Ba_2 Cu_3 O_x, Y;$ $Ba_2 Cu_3 O_3;$ $Bi_{2.15} Sr_{1.88} Ca_{1.7} Cu_2 O_{8.8};$ $Ca_{(2-x)} Sr_x Cu O_x$ and $Bi_2 Sr_2 Cu O_x$. Even though the last three compounds are made according to appellants' teaching they do not come within the scope of the claims allowed by the examiner in the answer since they do not include a rare earth or a group IIIB element. Moreover, in the answer the examiner quotes from the preface of the Poole article which states in part at A3: "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the

principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO. and YBaCuO has emerged". The first and third of these compositions does not come within the scope of the claims allowed by the examiner in the answer even though Poole states that they are easy to make following the general principals of ceramic science as taught by appellants. Other data supporting appellants view is reported in the Review Article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a $T_c < 26^\circ\text{K}$. Those twelve do not contain one or more of a rare earth, a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants teaching without undue experimentation. Appellants request remand for the examiner to consider this data in response to the examiner's new ground for rejection.

At page 21 of the answer, the examiner comments in regard to the claims rejected under 35 UCS 112, second paragraph, the examiner states that "[n]ote the Examiner declines to comment on appellants remarks regarding the after-final submissions which have not been entered or considered by the examiner." These unentered after final submissions provide evidence that the

terminology "perovskite-like", "perovskite-type", and "rare-earth-like" were understood by persons of skill in the art prior to appellants' filing date. This evidence is in addition to evidence previously submitted to show that these terms were well understood in the art. Thus this new evidence is not directed to any new issues but is additional evidence on the same issue. Prior to the Final Action the undersigned attorney requested the examiner to specify what information was needed to convince the examiner that these terms were well understood in the art. The examiner did not provide any guidance to appellants. Thus a trial and error approach was used to see if what was submitted was sufficient to convince the examiner. The examiner again in the Final Action indicated he was not convinced and appellants submitted additional evidence in the after final submissions. Some of the additional evidence is issued US patents having claims containing the identical terminology which the examiner finds indefinite. Other evidence is issued US patents using similar terminology in issued claims indicates that the use of such terminology in US patent claims is standard USPTO practice. Since the examiner would provide appellants no guidance on what would convince the examiner that these terms were understood by persons of skill in the art, appellants request remand for these after final submissions to be entered and considered.

In addition appellants request remand for the following reasons. After the final action which is the basis of this appeal there was a change in examiner. In the answer the examiner withdrew the prior art rejections over arguments

presented by appellants long before the Final Action. In the answer the rejection under 35 USC 112, first paragraph, was modified to allow broader claims than the single narrow claims allowed in the Final Action. The modification of 35 USC 112, first paragraph, rejection was based on arguments presented by appellants long before the Final Action. Appellants believe that further progress in either resolving all the issues remaining in this appeal or substantially simplifying the issues in this appeal can be made by remanding this application to the new examiner.

SUMMARY OF ARGUMENT IN THIS REPLY BRIEF

***THE EXAMINER HAS NOT REBUTTED APPELLANTS
CLAIM OF PRIORITY***

In the answer the examiner has not rebutted appellants' arguments in support of their claim of priority. Therefore, appellants request the board to grant appellants' claim of priority

***REJECTIONS UNDER 35 USC 102 AND 103 NECESSARILY
REQUIRES THAT ALL CLAIMS ARE FULLY ENABLED***

The examiner has withdrawn the rejections under 35 USC 102 and 103 over the Asahi Shinbum article since appellants have shown that they conceived prior to the date of this article and were diligent to a reduction to practice. The examiner has not commented on nor rebutted appellants' argument that in rejecting claims under 35 USC 102 and 103 over the Asahi Shinbum article, the examiner necessarily concludes that appellants' claims are fully enabled. The Asahi Shinbum article refers to appellants' work which was reported in their original article which is incorporated by reference in appellants' specification. Since appellants' original article is the only information enabling the Asahi Shinbum article, it logically follows that the examiner necessarily concludes that all appellants' claims are fully enabled.

**OBJECTION TO SPECIFICATION AND REJECTION OF CLAIMS
UNDER 35 USC 112, FIRST PARAGRAPH
THE EXAMINER HAS FAILED TO MEET HIS BURDEN OF PROOF**

The only support for the objection to the specification and rejection of claims as not enabled under 35 USC 112, first paragraph, is the examiner's unsupported statement that the field of high T_c superconductivity is unpredictable, the examiner's unsupported statement that the theoretical mechanism of superconductivity in these materials was not well understood, and three examples in applicants' specification that show metal oxides having a T_c < 26°K. One of these examples has an onset at 26°K. The examiner provides no extrinsic evidence to support the examiner's position of nonenablement. Applicants have submitted five affidavits of experts rebutting the examiner's position of nonenablement, the article by Rao et al. and the book by Poole et al. which clearly states that it is easy to fabricate high T_c materials. Moreover, the book by Poole, the Affidavit of Duncombe and the article by Rao shows numerous examples of high T_c metal oxides fabricated according to appellants' teaching which do not fall within the scope of the claims allowed by the examiner but do fall within the scope of the claims which have not been allowed by the examiner. The examiner has not rebutted appellants' application of case law which holds that 35 USC 112, first paragraph, permits claims to read on inoperable species. Notwithstanding, appellant's claims do not read on any inoperative species. Under *In re Angstadt* 190 USPQ 219, to sustain a rejection

under 35 USC 112, first paragraph, it is the examiner's burden to show that a person of skill in the art must engage in undue experimentation or require ingenuity beyond that expected of a person of skill in the art to practice the claimed invention. According to *In re Wands* 8 USPQ2d 1400, an application does not fail to meet the 35 USC 112 enablement requirement even though experimentation is needed to determine samples useful to practice the claimed invention when the experimentation is not undue. The examiner has not meet his burden under 35 USC 112, first paragraph, as articulated in *In re Angstadt* and *In re Wands*. Moreover under *In re Angstadt*, providing the examples in appellants' specification with a $T_c < 26^\circ\text{K}$ is commendable frankness and part of appellants' teaching on how to select a high T_c material. *In re Angstadt* and *In re Wands* hold that a claim is enabled if undue experimentation is not needed to determine if a particular species within the scope of the claim is effective to practice the claimed invention. This is the situation in the present application and the examiner has not rebutted appellants showing that only routine experimentation is needed to fabricate materials useful to practice appellants' invention. It is appellants' view that there can be no question that the record as a whole supports appellants' view that all the claims are fully enabled. Thus, appellants request the board to reverse the rejection to the specification and the rejection of claims under 35 USC 112, first paragraph.

**THE EXAMINER HAS NOT REBUTTED APPELLANTS'
PROOF THAT THE TERMINOLOGY OF THE CLAIMS REJECTED
UNDER 35 USC 112, SECOND PARAGRAPH,
ARE UNDERSTOOD BY PERSONS OF SKILL IN THE ART**

The examiners' rejection of claims as indefinite under 35 U.S.C. 112, second paragraph, for using terminology, such as "rare-earth like", "perovskite-like" and "perovskite-type" is a clear error since there are many issued patents having claims using terminology which is a combination of "-type", and "-like " and there are issued United States Patents having claims including the exact terminology objected to by the examiner. The examiner has given no reasons why the claims in the instant application are indefinite because of terminology using "-type" and "-like" while they are definite in the many cited issued patents. In the answer, the examiner has not rebutted appellants' arguments in the brief. Appellants' have provided extensive proof that this terminology was understood by persons of skill in the art at the time appellants published their original article. Moreover, appellants' original article was published about eight months before the filing date of the first application in the lineage of the present application. Since appellants used this terminology in their original article, the use of this terminology was part of the vernacular of persons of skill in the art and is thus understood by persons of skill in the art as of the earliest filing date of the instant application. The book by Poole

acknowledges this and uses this terminology. Thus appellants request the board to reverse the rejection of claims under 35 USC 112, second paragraph.

DETAILED ARGUMENT IN THIS REPLY BRIEF

Status of Claims

Claims 24-26, 86-90, 96-177 are pending.

Claim 136 was allowed at the time of Final Rejection. Claims 114-116, 119-121, 124-126, 132, 133, 137, 138, 143, 144, 146, 148, 152-157, 160-163, 167, 168, 171, 172 and 173 have been subsequently allowed in the examiner's answer.

Claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 remain rejected under 35 U.S.C. 112, first paragraph.

Claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 remain rejected under 35 U.S.C. 112, second paragraph.

Status of Amendments After Final

In appellant's original Brief filed 7/1/99, at page 4, reference was made to an after-final submission filed 12/14/98. In the Substituted Brief filed 1/18/00 no reference is made to this 12/14/98 after final submission since appellant s have determined that the original Brief incorrectly referred to thi s 12/14/98 after final submission. Accordingly, appellants acknowledge the record to be complete with respect to after-final submissions as delineated by appellant in the Substitute Brief filed 1/18/00. (Hereinafter Brief refers to the Subst itute Brief filed 1/18/2000).

Issues

In view of the claims allowed in response to appellant's Substitute Brief, appellants agree with the examiner's new statements of the issues.

Are claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 not enabled under 35 U.S.C. 112, first paragraph?

Are claims 86, 87, 96-108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 indefinite under 35 U.S.C. 112, second paragraph?

The 35 USC 102/103 Rejections Withdrawn In View of Appellants Argument Presented Prior to the Final Rejection

Applicant acknowledge the examiner's statement that "[t]he prior art rejection over Asahi Shinbum, International Satellite Edition (London) November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in view of applicant's remarks appearing at pages 39-44 of the supplemental response filed 8/5/99." Applicants respectfully submit that the examiner has not withdrawn the rejection but has found the rejection moot in view of the fact that the examiner has agreed that appellant has sufficiently demonstrated conception in the United States before the publication date of the Asahi Shinbum article and diligence to a reduction to practice. Appellants note that on December 3, 1998, Appellants petitioned for withdrawal of the final rejection since the examiner in the Final Action did not respond to Appellants' request for reasons why the examiner did not find that appellants effectively swore behind the date of the

Asahi Shinbum article in the Substitute Amendment dated March 6, 1997. That petition was denied by decision dated February 8, 1999 of Richard V. Fisher, Director Group 1700. The argument presented in the Brief on pages 39-44 in response to which the examiner has withdrawn the 35 USC 102/103 rejections over the Asahi Shinbum article is essentially identical to that presented in the petition to withdraw the Final Rejection and in response filed December 3, 1998. The decision not to withdraw the Final Rejection and not to withdraw the 35 USC 102/103 rejection over the Asahi Shinbum article required that appellants invest substantial time, effort and cost to prepare the argument presented in the Brief at pages 21-51.

***The Examiner Has Not Rebutted Appellants'
Claim of Priority to the Priority Document***

Appellants disagree with the examiner statement "Accordingly, the issue of claims 24-26, 86-90, 96-135 and 137-177 being supported by the priority document is believed moot in view of the withdrawal of the prior art rejections." Support for claims in a priority document is a separate and distinct issue from whether the claims are anticipated by a reference under 35 USC 102 or obvious over a reference under 35 USC 103. Therefore, the issue of claims 24-26, 86-90, 96-135 and 137-177 being supported by the priority document is not moot in view of the withdrawal of the prior art rejections. Since the examiner did not rebut applicants detailed and specific argument rebutting the examiners view that appellants' claims are not supported by the priority document, appellants

request the board to reverse the examiner and grant applicants claim of priority to the priority document.

Grouping of Claims

In response to applicants grouping of the claims in the brief the examiner states:

The appellant's statement in the brief that certain claims do not stand or fall together is not agreed with because appellant merely states "Each claim is appealed individually" but fails to present any detailed reasoning in support of such a statement.

Appellants disagree with the examiner that they have failed to present any detailed reasoning in support of their statement that "Each claim is appealed individually." Specific arguments as to each claim are given on pages 114- 173 of the brief. Since the examiner has not commented on nor rebutted any of these arguments, appellants are entitled to have each claim appealed individually.

The Examiner Has Not Rebutted Appellants' Argument That The Prior Art Rejections Necessarily Require That All Of Appellants' Claims Rejected Under 35 USC 120/103 Are Fully Enabled

In paragraph 9 of the Answer entitled "Prior Art of Record" the examiner states "No prior art is relied upon by the examiner in the rejection of the claims under appeal". Applicants disagree. Claims 24-26, 86-90, 96-135 and 137-177

have been rejected as anticipated under 35 USC 102(a) by the Asahi Shinbum article, and claims 24-26, 86-90, 96-135 and 137-177 have been rejected as obvious under 35 USC 103(a) in view of the Asahi Shinbum article. These rejections have not in fact been withdrawn, but, as stated above, have in fact been found to be moot.

In the Final Action all the claims, except claim 136, were rejected either under 35 USC 102 or 35 USC 103 over the Asahi Shinbum article. Thus in the Final Action, the Examiner is stating that everything within applicants' non-allowed claims rejected under 35 USC 102 over this article, is found in the Asahi Shinbum article and a person of skill in the art can practice the invention of applicants' claims rejected under 35 USC 102 with what is taught in the Asahi Shinbum article alone. Moreover, in the Final Action, the examiner is stating that all the claims rejected under 35 USC 103 over the Asahi Shinbum article alone can be practiced by a person of skill in the art with what is taught in the Asahi Shinbum article in combination with what is known to a person of skill in the art. All of applicants' claims rejected over the Asahi Shinbum article are dominant to (or generic to) the one claim, claim 136, allowed in the Final Action. Thus by stating that all the non-allowed claims are anticipated or obvious over the Asahi Shinbum article alone, the Examiner is stating that a person of skill in the art needs nothing more than what is taught in the Asahi Shinbum article or what is taught therein in combination with what is known to a person of skill in the art to practice that part of each of appellants non-allowed claims which does not

overlap applicants' allowed claim. Thus, it logically follows from the 35 USC 102/103 rejections that all of appellants' claims are fully enabled.

The Asahi Shinbum article states in the first paragraph:

A new ceramic with a very high T_c of 30K of the superconducting transition has been found. The possibility of high T_c - superconductivity has been reported by scientists in Switzerland this spring. The group of Prof. Shoji TANAKA, Dept. Appl. Phys. Faculty of Engineering at the University of Tokyo confirmed in November, that this is true.

and in the second paragraph:

The ceramic newly discovered, is an oxide compound of La and Cu with Barium which has a structure of the so-called perovskite and shows metal-like properties. Prof. Tanaka's laboratory confirmed that this material shows diamagnetism (Meisner effect) which is the most important indication of the existence of superconductivity.

The Swiss scientist are the inventors of the present application. Thus this clearly refers to applicants work which was reported in appellants' article which is incorporated by reference in the present application . These passages say that Prof. Tanaka confirmed applicants work. The newly discovered ceramic

referred to in the article is the ceramic reported on in appellants' article. It is thus clear that for the examiner to have rejected appellants claim over the Asahi Shinbum article under 35 USC 102 or 35 USC 103, the examiner necessarily had to find that appellants' article fully enabled their claims.

In the answer the examiner has not commented on nor rebutted these arguments. In appellants' brief at pages 21-22 and at pages 49-51 appellants apply these arguments in detail to the rejection of applicants claims under 35 USC 102 and 35 USC 103, respectively. The examiner, therefore, must be taken to agree with applicants argument in the brief that their teaching has fully enabled all of their claims.

At pages 50-52, at the beginning of appellants' arguments in regard to the objections and rejection based on 35 USC 112, first paragraph, appellants' have repeated these arguments, that is that the 35 USC 102/103 rejections over the Asahi Shinbum article logically requires that all of appellants' claims are fully enabled by appellants' teaching. The examiner has again not responded nor rebutted them. The examiner, therefore, must be taken to agree with applicants argument in the brief that their teaching has fully enabled all of their claims.

The examiners rejections under 35 USC 102 and 103 over the Asahi Shinbum articles have been maintained since the Office Action dated August 26, 1992. Thus the examiner has maintained the view that all of appellants' claims

are fully enabled for about eight years. In view of the fact that the examiner has not rebutted applicants' arguments the Board does not have to consider the examiner's objection under 35 USC 112, first paragraph, that the specification fails to provide an enabling disclosure commensurate with the scope of the claims and the rejections of claims under 35 USC 112, first paragraphs, for lack of enablement.

In summary, all of applicants' claims on appeal, except for claim 136, were originally rejected under 35 USC 102 and/or 103 as being anticipated or obvious over the Asahi Sinbum article which only stated that a professor in Japan reproduced applicants work reported in applicants' published article which was incorporated by reference in the present application. The only logical conclusion from these rejections is that applicants' teaching fully enabled the claims originally rejected under 35 USC 102 and/or 103 which is all of applicants claims except for claim 136. The examiner in the answer has not rebutted this. The examiner has, therefore, conceded, and is estopped from denying, that all of appellants' claims are fully enabled by applicants' teaching.

Grounds For Rejection

In paragraph 10 of the answer entitled "Grounds of Rejection" the examiner as stated above introduces a new ground for rejection . The examiner states:

The following ground(s) of rejection are applicable to the

appealed claims:

The specification is objected to under 35 U.S.C. § 112, first paragraph, as failing to provide an enabling disclosure commensurate with the scope of the claims.

In support of this statement the examiner states:

The present specification is **deemed** to be enabled only for compositions comprising a transition metal oxide containing at least a) an alkaline earth element and b) a rare-earth element or Group IIIB element. The art of high temperature (above 30°K) superconductors is an extremely unpredictable one. Small changes in composition can result in dramatic changes in or loss of superconducting properties. The amount and type of examples necessary to support broad claims increases as the predictability of the art decreases. Claims broad enough to cover a large number of compositions that do not exhibit the desired properties fail to satisfy the requirements of 35 U.S.C. 112. Merely reciting a desired result does not overcome this failure. In particular, the question arises: Will any layered perovskite material exhibit superconductivity.

Except for the first sentence which is the new ground for rejection , Appellants have responded in detail to these comments in the brief. A large number of examples are needed to support a broad claim in an unpredictable art only if a person of skill in the art has to engage in undue experimentation to determine embodiments not specifically recited in appellants' teachings. It is the examiner's burden to show that undue experimentation is necessary. The examiner has presented no extrinsic evidence that a person of skill in the art would have to engage in undue experimentation. The examiner has stated without support that the art of high temperative superconductivity is an extremely unpredictable one. Appellants have not merely stated a desired result as clearly shown by the five affidavits submitted by experts in the field , the Poole book and the Rao article. And it is not necessary for any layered perov skite to work to satisfy 35 USC 112, first paragraph, it is only necessary that they can be determined without undue experimentation.

The examiner restates without support that "It should be noted that at the time the invention was made, the theoretical mechanism of superconductivity in these materials was not well understood. That mechanism still is not understood." Appellants note that the theory of superconductivity has been understood for some time. For example, at page 20 of the brief the book by Von Laue is referred to. This book was published in English in 1952 and presents a comprehensive theory of superconductivity. The entire text of this book is

included in Attachment A of this reply brief. Notwithstanding, for a claim to be enabled under section 112, it does not require an understanding of the theory. The examiner then conclusorily states "Accordingly, there appears to be little factual or theoretical basis for extending the scope of the claims much beyond the proportions and materials actually demonstrated to exhibit high temperature superconductivity". This statement is clearly inconsistent with *In re Angstadt* 190 USPQ 219 and *In re Wands* 8 USPQ2d 1400 which hold that to satisfy the first paragraph of 35 USC 112 it is only necessary that a person of skill in the art not exercise undue experimentation to make samples that come within the scope of the applicants claims. Appellants have clearly shown that only routine experimentation is needed to fabricate samples to practice applicants claimed invention. The examiner has not denied, nor rebutted this. The examiner again incorrectly cites *Brenner v. Morrison* stating a "patent is not a hunting license. It is not a reward for the search, but a reward for its successful conclusion". As stated in the brief, this quote applies to utility not to enablement and is thus incorrectly cited by the examiner.

Reply to Answer Paragraph (11) Entitled "Response to Argument"

The examiner states:

As discussed above in section 6 Issues, the prior art rejection over Asahi Shinbum, International Satellite Edition (London), November 28, 1986 (hereinafter, "the Asahi Shinbum article") is withdrawn in

view of applicant's remarks. It is believed that the withdrawn of the prior art rejection addresses each of applicant's remarks appearing at pages 7-51 and pages 114-173 of the Substitute Brief filed 1/18/00 (paper #89).

Applicants disagree with the examiner that "that the withdrawn of the prior art rejection addresses each of applicant's remarks appearing at pages 7-51 and pages 114-173 of the Substitute Brief". This is only true in so far as these pages contains arguments in rebuttal of the rejections under 35 USC 102 and 103 which have been rendered moot since the examiner has been convinced by their argument submitted prior to the Final Action that appellants conceived their invention in the United States prior to the date of the Asahi Sinbum article and were diligent to a reduction to practice. As noted above, the examiner has not rebutted applicants argument that the 35 USC 102 and 103 rejections over the Asahi Sinbum article necessarily requires that applicants have fully enabled all their claims. Moreover, pages 114-173 have arguments in support of the patentability of each of the claims. The examiner has not specifically responded nor rebutted any of these specific arguments. Thus, these specific arguments are not rendered moot and must be considered by the Board.

Appellants acknowledge that the rejection under under 35 USC 112, first paragraph, in the Final Office Action, has been modified in scope in the answer. The examiner has determined that the instant specification is enabled for

compositions comprising a transition metal oxide containing an alkaline earth element and a rare-earth or Group IIIB element. Appellants disagree with this. As shown below there are numerous materials made according to appellants' teaching which do not come within the scope of the claims allowed by the examiner in the answer.

The examiner logically inconsistently with the 35 USC 102/103 rejection of appellants' claims objects to appellants' specification and rejects claims as not enabled under 35 USC 112, first paragraph. With respect to the remaining claims rejected under 35 U.S.C. 112, first paragraph, the examiners referring to:

1. appellant's remarks appearing at pages 52-101 of the Substitute Brief;
2. appellants' arguments filed 1/18/00;
3. the Affidavits filed September 29, 1995, January 3, 1996 (paper nos. 49 and 52);
4. the after-final submissions December 15, 1998: (1.132 Declarations of Mitzi, Tsuei, Dinger, Shaw and Duncombe) (Advisory mailed 2/25/99 (Paper 77E))

states they "have been fully considered but they are not **deemed** to be persuasive." (emphasis added)

As noted at page 8 of the specification **deemed** means to have an opinion: believe. The examiner uses the word "deemed" often in the examiner's answer, that is, it is the examiner's opinion or belief unsupported by any factual

evidence. Applicants view is that the examiner's use of the word "deemed" necessarily requires a finding that the examiner has not met the examiner's burden for establishing a case of lack of enablement since the argument is only based on the examiner's opinion or belief and not on any significant factual evidence. As noted at page 64 of the Brief In re Angstadt states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not enabling. In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975).

Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under Armbruster; this court has never held that evidence of the necessity for *any* experimentation, however slight, is sufficient to require the applicant to prove that the type and amount of experimentation needed is not undue.

The examiner in the answer has not commented on applicants arguments rebutting the examiner's reasons for non-enablement. The examiner has not satisfied his burden of giving reasons, supported by the record as a whole, why the specification is not enabling. Applicants have provided extensive evidence that to practice applicants claimed invention does not require undue experimentation but only requires routine experimentation. That only routine experimentation is needed to practice applicants claimed invention is shown for example by the affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe, the article of Rao et al. and the book of Poole et al. all of which state or show it is

straight forward to use the general principles of ceramic science to make high T_c transition metal oxide superconductors which is appellants' teaching.

The examiner has not rebutted this but merely **deems** applicants specification to be non-enabling, that is, it is the examiners opinion or belief that applicants specification is nonenabling.

The examiner further states:

The additional case law and arguments by the applicants have been duly noted. For the reasons that follow, however, the record as a whole is **deemed** to support the initial determination that the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed. (Emphasis Added)

The examiner has not commented upon nor rebutted appellants' application of these cases to the facts of the present claims on appeal. The examiner merely **deems** (that is in the examiners opinion or belief) "the originally filed disclosure would not have enabled one skilled in the art to make and use the invention to the scope that it is presently claimed." The examiner presents no intrinsic or extrinsic facts to support the examiner's opinion or belief. The examiner has, therefore, not met his burden "of giving reasons, supported

by the record as a whole, why the specification is not enabling." In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). Merely stating without evidentiary support that the art of high T_c superconductivity is unpredictable and stating without support that the theoretical mechanism is not understood does not satisfy the examiner's burden.

The examiner further states:

The applicants quote several passages from their specification at pp. 13-15 of their September 29, 1995 Amendment, but the issue is the scope of enablement, not support. The present disclosure may or may not provide support for particular embodiments, but the issue here is the scope to which that disclosure would have taught one skilled in the art how to make and use a composition which shows the onset of superconductivity at above 26°K. Construed in light of that issue, the invention is not **deemed** to have been fully enabled by the disclosure to the extent presently claimed. (Emphasis Added)

Again the examiner **deems** appellants' claims not enabled. At page 54 of the brief appellants state "Applicants do not have to provide experimental results for every composition that fall within the scope of their claims when a person of skill in the art exercising routine experimentation has a reasonable expectation of success following applicants teaching to achieve a composition through which

can be flowed a superconducting current according to the teaching of Applicants' specification." The examiner has not commented upon nor rebutted this argument. As extensively shown in the brief, it is a matter of routine experimentation to make the compounds which come within the scope of appellants' claims. The examiner has not commented on nor rebutted this. The examiner merely states "Construed in light of that issue, the invention is not **deemed** to have been fully enabled by the disclosure to the extent presently claimed." Again, the examiner is merely stating without any intrinsic or extrinsic evidence that it is the examiners' opinion or belief that the invention is not fully enabled by the disclosure to the extent presently claimed. Again the examiner has not met his burden "of giving reasons, supported by the record as a whole, why the specification is not enabling." In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975).

The examiner further states:

(1) In their September 29, 1995 Amendment, the applicants argue that their disclosure refers to "the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen", and list several species such as " $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ " which they indicate are found in the present disclosure.

(2) Notwithstanding that argument, it still does not follow that the invention is fully enabled for the scope presently claimed. The claims include formulae which are much broader than the RE-TM-0 formula cited in the disclosure. Claim 24 recites "a transition metal oxide", claim 88 "a composition", and claim 96 "a copper-oxide compound".

Appellants note that their disclosure is not limited to any particular formula as implied by the examiner. See for example the Summary of The Invention which states at page 7, lines 2-5, "In general, the compositors are characterized as mixed transition metal oxide systems where the transition metal can exhibit multivalent behavior".

As stated in the brief at pages 54-55:

According to *In re Angstadt* 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. The CCPA states:

To require such a complete disclosure would apparently necessitate a patent application or applications with "thousands" of examples or the disclosure of "thousands" of catalysts along with information as to whether each exhibits catalytic behavior resulting in the production of

hydroperoxides. More importantly, such a requirement would force an inventor seeking adequate patent protection to carry out a prohibitive number of actual experiments. This would tend to discourage inventors from filing patent applications in an unpredictable area since the patent claims would have to be limited to those embodiments which are expressly disclosed. A potential infringer could readily avoid "literal" infringement of such claims by merely finding another analogous catalyst complex which could be used in "forming hydroperoxides."

This is exactly the situation in the present application. If applicants are limited to the claims that are allowed by the examiner, a potential infringer could readily avoid "literal" infringement of such claims by merely finding, through routine experimentation, other transition metal oxides having a high T_c . As shown below there are numerous materials made according to appellants' teaching which do not come within the scope of the claims allowed by the examiner in the answer.

The examiner further essentially repeats what was stated in the Final Action:

The present specification actually shows that known forms of a "transition metal oxide", "a composition", and "a copper-oxide compound" do not show the onset of superconductivity at above

26° K. At p. 3, line 20, through p. 4, line 9, of their disclosure, the applicants state that the prior art includes a "Li-Ti-O system with superconducting onsets as high as 13.7°K." Official Notice is taken of the well-known fact that Ti is a transition metal. That disclosure also refers to "a second, nonconducting CuO phase" at p. 14, line 18.

In response to this appellant stated at page 7 in the brief:

Applicants claims are directed to "transition metal oxides", "a composition" and "a copper-oxide compound" having a T_c in excess of 26°K which is carrying a superconducting current. Applicants claims do not include in the claimed method compositions having $T_c < 26^\circ\text{K}$. Thus the examples on page 3, line 20 - page 4, line 9, are not included in applicants claims. That these are transition metal oxides having $T_c < 26^\circ\text{K}$ does not mean that Applicants' claims directed to transition metal oxides, compositions and copper oxides having $T_c > 26^\circ\text{K}$ are not enabled. Applicants provide the teaching on how to fabricate such oxides having $T_c > 26^\circ\text{K}$. The "second non-conducting CuO phase" referred to at page 14, line 18, again does not mean that applicants claims are not enabled. Applicants' statements at page 14 is part of applicants teaching on how to achieve an oxide having a $T_c > 26^\circ\text{K}$. The Examiner is

attempting to use Applicants' complete description of their teaching to show lack of enablement when, in fact, this complete teaching provides full enablement by showing how samples are and are not to be prepared. Applicants have claimed their invention functionally, that is, as a method of use so the Applicants' claim do not read on inoperable species. What the Examiner "**seems to be obsessed with is the thought of [transition metal oxides] which won't work to produce the intended result. Applicants have enabled those of skill in the art to see that this is a real possibility which is commendable frankness in a disclosure.**"

In re Angstadt, Supra. (Emphasis Added)

The examiner has not commented on appellants citation of In re Angstadt in support of their position which has been presented as bolded and underlined above. The examiner seems to be of the view that the first paragraph of 35 USC 112 requires absolute certainty. As stated in the brief at pages 54-55 according to In re Angstadt 190 USPQ 214, 218 in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. In the answer the examiner has not responded nor rebutted appellants' argument.

As stated by appellants in the brief, in particular at page 63, according to In re Angstadt all that is necessary is that the experimentation required to determine which combinations have the desired result (i.e. T_c greater than 26°K)

can be produced without undue experimentation and would not "require ingenuity beyond that to be expected of one of ordinary skill in the art". 190 USPQ, 214, 218 in re Field v. Connover 170 USPQ, 276, 279 (1971).

Appellants have provided extensive evidence that transition metal oxides can be made according to appellants' teaching without undue experimentation and without requiring "ingenuity beyond that to be expected of one of ordinary skill in the art". In the answer, the examiner has not responded to nor rebutted appellants' arguments.

The examiner further states:

Accordingly, the present disclosure is not **deemed** to have been fully enabling with respect to the "transition metal oxide" of claim 24, the "composition" of claim 88,, or the "copper-oxide compound" of claim 96. (Emphasis added.)

Again without facts or acceptable reasons the examiner "**deems**" appellants' claims not enabled and for the reasons given above appellants disagree. Appellants discovered that metal oxides have $T_c > 26^\circ\text{K}$ that is why they were awarded a Nobel Prize. With respect to the transition metal oxide of claim 24, the "composition" of claim 88 and the "copper-oxide compound" of claim 88, there is no evidence in the record that a person of skill in the art cannot practice the claimed invention without undue experimentation. The only

attempt made by the examiner to factually support the examiner's statement that the claims "are **deemed** not enabled" are the examples provided by appellants which show $T_c < 26^\circ\text{K}$. Appellants provide this teaching so that a person of skill in the art will be fully informed on how to practice appellants invention. In this regard the examiner states:

The examples at p. 18, lines 1-20, of the present specification further substantiates the finding that the invention is not fully enabled for the scope presently claimed. With a 1:1 ratio of (Ba, La) to Cu and an x value of 0.02, the La-Ba-Cu-O form (i.e., "RE-AE-TM-0", per p. 8, line 11) shows no superconductivity". With a 2:1 ratio of (Ba, La) to Cu and an x value of 0.15, the La-Ba-Cu-O form shows an onset of superconductivity at " $T_c = 26^\circ\text{K}$ ". It should be noted, however, that all of the claims in this application require the critical temperature (T_c) to be "in excess of 26°K " or "greater than 26°K ".

Appellants note that examiner states that "the present specification **further substantiates** the finding that the invention is not fully enabled" (Emphasis added) misrepresents the examiner's argument up to this point since up to this point the examiner has only used the unsupported statements that the theory of high T_c art is very unpredictable and that the theory of high T_c in these

materials is not understood. These unsupported statements do not substantiate anything and should be disregarded by the Board.

Appellants note that the examiner cites 3 examples from applicants' specification which are transition metal oxides which do not have a $T_c > 26^\circ\text{K}$: 1) a Li-Ti-O system with superconducting onsets as high as 13.7°K (cited at p. 3, line 20, through p. 4, line 9) , 2) the 1:1 ratio with an $x=0.02$ sample cited on page 18, line 7, which did not show superconductivity, and 3) the 2:1 composition with $x=0.15$ with a resistivity drop that occurs at 26°K . In appellants view the examiner is making a specious argument in regards to the third example. Thus there are only two examples upon which the examiner is "**deeming**" applicants claims not enabled. The examiner seems to be of the view that an applicants' must have 100% predictability. Appellants and the courts disagree. The fact that there are transition metal oxides having $T_c < 26^\circ\text{K}$ does not mean that applicants have not fully enabled their claimed invention. If only routine experimentation is needed to determine which transition metal oxides have $T_c > 26^\circ\text{K}$, without requiring ingenuity beyond that to be expected of one of ordinary skill in the art, then applicants' disclosure enables applicants' claims. In the brief at page 65 appellants note that In re Angstadt states at 190 USPQ 219:

We note that the PTO has the burden of giving reasons, supported by the record as a whole, why the specification is not

enabling. In re Armbruster, 512 F.2d 676, 185 USPQ 152 (CCPA 1975). **Showing that the disclosure entails undue experimentation is part of the PTO's initial burden under Armbruster; this court has never held that evidence of the necessity for any experimentation, however slight, is sufficient to require the applicant to prove that the type and amount of experimentation needed is not undue. ... Without undue experimentation or effort or expense the combinations which do not work will readily be discovered and, of course, nobody will use them and the claims do not cover them. The [examiner] wants appellants to make everything predictable in advance, which is impracticable and unreasonable. ... The key word is "undue," not "experimentation." (Emphasis Added)**

The examiner has not commented on nor rebutted this argument. The examiner's statement that "the present disclosure is not **deemed** to have been fully enabling" is not sufficient to meet the examiner's burden under In re Armbruster and the examiner has thus failed to establish that applicants claims are not enabled. "Appellants do not have to make everything predictable in advance" where, as here, the experimentation to make samples that can be used within the scope of the appellants' claims is not undue.

The examiner further states:

The applicants also have submitted three affidavits attesting to the applicants' status as the discoverers of materials that superconduct $> 26^{\circ}\text{K}$. Each of the affidavits further states that "all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner (way)". Each of the affidavits add "(t)hat once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K , such a person of skill in the art, using the techniques described in the (present) application, which includes all known principles of ceramic fabrication, can make the transition metal oxide compositions encompassed by (the present) claims ... without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art." All three affiants apparently are the employees of the assignee of the present application. Those affidavits do not set forth particular facts to support the conclusions that all superconductors based on the work behave in the same way and that one skilled in applicants' work behave in the same way and that one skilled in the art can make those superconductors without undue experimentation. Conclusory statements in an affidavit or specification do not provide the factual evidence needed for patentability.

The examiner has incorrectly stated that appellants have produced three affidavits. Appellants have produced five affidavits of affiants who are employed at the IBM, Thomas J. Watson Research Center. The affidavits of Shaw and Duncombe were reviewed and considered in paper 77E, page 2 and are referred to at page 10 of the answer. The affidavits of Mitzi, Dinger, Tsuei, Shaw and Duncombe and the book of Poole et al. state it is straight forward to use the general principles of ceramic science to make high T_c transition metal oxide superconductors following appellants' teaching. The book of Poole et al. and the affidavit of Duncombe show numerous example of high T_c superconductors produced according to applicants teaching. The affidavits of Shaw and Duncombe cites numerous books and articles which provide the general teaching of ceramic science at the time of and prior to the filing date of the present application. The affidavit of Duncombe also provides several hundred pages copied from Mr. Duncombe's notebooks starting from before appellants' filing date showing the fabrication of numerous samples. In regards to these pages, Mr. Duncombe states "I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1998 and in technical notebook V with entries continuing from June 7, 1988 to May 1989." Mr. Duncombe's affidavit list some of the compounds prepared using the general principles of ceramic science: $Y_1 Ba_2 Cu_3 O_x$; $Y_1 Ba_2 Cu_3 O_3$; $Bi_{2.15} Sr_{1.98} Ca_{1.7} Cu_2 O_{\delta+8}$; $Ca_{(2-x)} Sr_x Cu O_x$ and $Bi_2 Sr_2 Cu O_x$. Appellants note that the last three examples do not come within the scope of the claims allowed by the examiner in the answer since

they do not contain a rare earth or group III B element. The examiner has not commented on the data in Mr. Duncombe's affidavit. Mr. Duncombe's affidavit provides direct evidence that these examples were made following appellants' teaching without undue experimentation. Moreover, in the answer the examiner quotes from the preface of the Poole article which states in part at A3 : "The unprecedented worldwide effort in superconductivity research that has taken place over the past two years has produced an enormous amount of experimental data on the properties of the copper oxide type materials that exhibit superconductivity above the temperature of liquid nitrogen. ... During this period a consistent experimental description of many of the properties of the principal superconducting compounds such as BiSrCaCuO, LaSrCuO, TlBaCaCuO. and YBaCuO has emerged". The first and third of these compositions does not come within the scope of the claims allowed by the examiner in the answer since they do not contain a rare earth or group III B element, even though Poole states that they are easy to make following the general principals of ceramic science as taught by appellants. Other data supporting appellants view is reported in the Review Article "Synthesis of Cuprate Superconductors" by Rao et al., IOP Publishing Ltd. 1993. A copy of this article is in Attachment C to the reply brief. This article lists in Table 1 the properties of 29 cuprate superconductors made according to appellants teaching. Twelve (#'s 1, 8-13, 16, 17, 20, 21, 27 and 28) of those listed do not come within the scope of the claims allowed by the examiner. Only three of the 29 have a $T_c < 26^\circ\text{K}$. Those twelve do not contain one or more of a rare earth,

a group IIIB element or an alkaline earth element. It is thus clear that broader claims than allowed in the answer should be allowed since it is clear that the allowed claims can be avoided following appellants teaching without undue experimentation. Appellants are entitled to claims which encompass these materials since they were made following appellants' teaching.

The article of Rao et al. in the first sentence of the introduction citing appellants' article - which is incorporated by reference in their application - acknowledges that appellants initiated the field of high Tc superconductivity. Appellants further note that the Rao article acknowledges that "a large variety of oxides" are prepared by the general principles of ceramic science and that appellants discovered that metal oxides are high Tc superconductors. Citing reference 5 therein - the book "New Directions in Solid State Chemistry", Rao et al. 1989 (Cambridge; Cambridge University Press) for which there is a 1986 edition which predates appellants filing date Rao (See Attachment B) - Rao et al. states:

Several methods of synthesis have been employed for preparing cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the

ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specifically noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distance in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed.

Reference 5 is another example of a reference to the general principles of ceramic science incorporated into appellants teaching. The Rao et al. article states that the 29 materials reported on in the article and fabricated in Table 1 are fabricated using the general principles of ceramic science. Moreover, the Rao article states that these materials are fabricated by what the Rao article calls the “ceramic method” which is the preferred embodiment in appellants specification, yet 12 of the 29 materials in Table 1 do not come within the scope of the claims allowed by the examiner in the answer. Thus known examples fabricated according to appellants’ teaching will not be literally infringed by the Rao, Duncombe and Poole examples.

The examiner further states:

Those affidavits do not overcome the non-enablement rejection.

The present specification discloses on its face that only certain oxide compositions of rare earth, alkaline earth, and transition metals made according to certain steps will superconduct at $> 26^{\circ}\text{K}$.

As stated above, In re Angstadt 190 USPQ 214, 218 held that in an unpredictable art, §112 does not require disclosure of a test with every species covered by a claim. As stated above, appellants note that the examiner has presented no extrinsic evidence that the art of high T_c superconductivity is unpredictable. It is the examiner's burden to show that a person of skill in the art would have to engage in undue experimentation to practice applicants' claimed invention. The examiner has clearly not done this. The only evidence that the examiner offers in support of his determination of nonenablement are three examples of metal oxide with $T_c < 26^{\circ}\text{K}$ which the appellants with commendable frankness have included in their specification. Appellants also note, as stated above, there are many other materials made according to appellants' teaching reported in the literature made following appellants teaching which do not come within the scope of the claims allowed in the examiner's answer.

The examiner further states:

Those affidavits are not **deemed** to shed light on the state of the art and enablement at the time the invention was made. One may know now of a material that superconducts at more than 26°K, but the affidavits do not establish the existence of that knowledge on the filing date for the present application. Even if the present application "includes all known principles of ceramic fabrication", those affidavits do not establish the level of skill in the ceramic art as of the filing date of that application.

The examiner stated to the contrary in paper 77E page 2, that "It is the examiner's maintained position that [the] general principles a ceramic fabrication were most certainly known prior to the filing date of the instant application." Thus the examiner acknowledges that the general principles of ceramic science were known prior to appellants filing date. There is no evidence in the record to indicate that anything more is needed to fabricate compositions which can be used to practice applicants' invention to the full scope that it is claimed in the present invention. To the contrary, appellants have shown numerous examples in the affidavits and references of samples fabricated according to appellants' teaching useful to practice their claimed invention. Notwithstanding, since the claims are method of use claims, appellants do not believe that they are required to provide a teaching of how to fabricate all compositions which may be used within the full scope of applicants' claimed invention.

The examiner acknowledges that the applicants are the pioneers in high temperature metal oxide superconductivity. However, the examiner states "The finding remains, nonetheless, that the disclosure is not fully enabling for the scope of the present claims". The examiner has not commented on appellants' comments in the brief that once applicants discovered high Tc in metal oxides, it was straight forward for others following appellants' teaching to make other examples of high Tc metal oxides. That appellants were the pioneers in Tc metal oxides is not the only issue. The relative ease of making other metal oxides is equally important. Applicants discovery is that metal oxides had high Tc. The fabrication techniques are not applicants discovery since these techniques, as acknowledged by the examiner, were well known prior to applicants discovery.

The examiner has cited seven decisions as providing the legal basis for this determination of non-enablement. In the brief appellants have extensively shown how these seven cases support appellants' position that they have fully enabled their claims. In the answer, the examiner has not rebutted appellants' extensive analysis of these cases and how they apply to the present invention to support appellants' view that appellants' claims are fully enabled. The examiner has not rebutted appellants arguments as to how the examiner has misapplied these cases to the present application. The examiner states "That case law speaks for itself". Applicants agree that the case law speaks for itself, that is, it

supports appellants' position that their claims are fully enabled. The examiner apparently means by this statement that the case law supports the examiner's position that the rejected claims are not enabled. The examiner has not attempted to show how the facts of the cited cases relate to the facts of the present application. The examiner has essentially taken statements out of context from these cases to support the examiner's view. However, when the cases are analyzed as appellants have done in the brief, it is clear that these cases support appellants view that their claims are fully enabled.

The MPEP SECTION---2164.01(a) entitled "Undue Experimentation Factors" citing In re Wands 8USPQ2d 1400 states:

There are many factors to be considered when determining whether there is sufficient evidence to support a determination that a disclosure does not satisfy the enablement requirement and whether any necessary experimentation is "undue." These factors include, but are not limited to:

- (A) The breadth of the claims;
- (B) The nature of the invention;
- (C) The state of the prior art;
- (D) The level of one of ordinary skill;
- (E) The level of predictability in the art;
- (F) The amount of direction provided by the inventor;
- (G) The existence of working examples; and
- (H) The quantity of experimentation needed to make or use the invention based on the content of the disclosure.

The examiner has not applied these factors. Appellants have shown that:

(A) Their claims are as broad as their discovery which is that metal oxides can carry a superconductive current for a $T_c > 26^\circ \text{K}$;

(B) The invention is easily practiced by a person of skill in the art;

(C) The state of the prior art clearly shows how to fabricate materials which can be used to practice appellants' invention;

(D) The level of one of ordinary skill in the art is not high since as stated in the Poole et al. book materials to practice appellants' invention are easily made and all that is needed to practice appellants' claimed invention is to cool the material below the T_c and to provide a current which will be a superconductive current. It has been well known how to do this since the discovery of superconductivity in 1911. (See page 1 of "Superconductivity" by M. Von Laue)

(E) There is no unpredictability in how to make materials to practice appellants' invention and there is no unpredictability in how to practice applicants' invention. The only unpredictability is which particular metal oxide will have a $T_c > 26^\circ \text{K}$. As extensively shown by appellants this is a matter of routine experimentation. The examiner has not denied nor rebutted this.;

(F) Appellants have provided extensive direction to make materials to practice their claimed invention. They have included all known principles of ceramic science. Also, as stated in the Poole book these materials are easily made. The examiner has not denied nor

rebutted this. The examiner has made no comment on the amount of direction provided by the appellants;

(G) Appellants have provided sufficient working examples and examples of metal oxides that have $T_c > 26^\circ\text{K}$ for a person of skill in the art to fabricate materials that can be used to practice appellants' claimed invention; and

(H) Appellants have shown that the quantity of experimentation needed to make samples to use the invention based on the content of the disclosure in the specification is routine experimentation.

The MPEP SECTION---2164.01(a) further states:

The fact that experimentation may be complex does not necessarily make it undue, if the art typically engages in such experimentation. In re Certain Limited-Charge Cell Culture Microcarriers, 221 USPQ 1165, 1174 (Int'l Trade Comm'n 1983), aff'd. sub nom., Massachusetts Institute of Technology v. A.B. Fortia, 774 F.2d 1104, 227 USPQ 428 (Fed. Cir. 1985).

See also In re Wands, 858 F.2d at 737, 8 USPQ2d at 1404. The test of enablement is not whether any experimentation is necessary, but whether, if experimentation is necessary, it is undue. In re Angstadt, 537 F.2d 498, 504, 190 USPQ 214, 219 (CCPA 1976). MPEP 2164

There is no statement by the examiner nor any evidence in the record that the experimentation to make materials to practice appellants' claimed invention

is complex or undue. But it is clear that even if the experimentation was complex to make samples to practice appellants' claimed invention it would not render appellants' claims not enabled since the art typically engages in the type of experimentation taught by appellants to make samples to practice their claimed invention.

The facts of *In re Wands* have similarity to the facts of the present application under appeal. The Court at 8 USPQ2d 1406 held that:

The nature of monoclonal antibody technology is that it involves screening hybridomas to determine which ones secrete antibody with desired characteristics. Practitioners of this art are prepared to screen negative hybridomas in order to find one that makes the desired antibody.

Correspondingly appellants have shown that the nature of high T_c technology is that it involves preparing samples to determine which ones have $T_c > 26^\circ\text{K}$ - the desired characteristic. Practitioners of this art are prepared to prepare samples in order to find one that have the desired T_c . Nothing more is required under *In re Wands*.

Appellants have shown that their specification is enabling with respect to the claims at issue and that there is considerable direction and guidance in the

specification; with respect to appellants' claimed invention there was a high level of skill in the art to fabricate samples at the time the application was filed; and all of the methods needed to practice the invention were well known. Thus appellants have shown that after considering all the factors related to the enablement issue, it would not require undue experimentation to obtain the materials needed to practice the claimed invention. The examiner has not denied nor rebutted this.

A conclusion of lack of enablement means that, based on the evidence regarding each of the above factors, the specification, at the time the application was filed, would not have taught one skilled in the art how to make and/or use the full scope of the claimed invention without undue experimentation. In *re Wright*, 999 F.2d 1557, 1562, 27 USPQ2d 1510, 1513 (Fed. Cir. 1993). It is the examiner's burden to show this and the examiner has clearly not done so.

The breadth of the claims was a factor considered in *Amgen v. Chugai Pharmaceutical Co.*, 927 F.2d 1200, 18 USPQ2d 1016 (Fed. Cir.), cert. denied, 502 U.S. 856 (1991). In the *Amgen* case, the patent claims were directed to a purified DNA sequence encoding polypeptides which are analogs of erythropoietin (EPO). The Court stated that:

Amgen has not enabled preparation of DNA sequences sufficient to support its all-encompassing claims. . . . [D]espite extensive statements in the specification concerning all the analogs of the

EPO gene that can be made, there is little enabling disclosure of particular analogs and how to make them. Details for preparing only a few EPO analog genes are disclosed. . . . This disclosure might well justify a generic claim encompassing these and similar analogs, but it represents inadequate support for Amgen's desire to claim all EPO gene analogs. There may be many other genetic sequences that code for EPO-type products. Amgen has told how to make and use only a few of them and is therefore not entitled to claim all of them. 927 F.2d at 1213-14, 18 USPQ2d at 1027.

In the present application appellants have provided a teaching (and proof thereof) of how to make all known high T_c materials useful to practice their claimed invention. As the Amgen court states this type of disclosure justifies a generic claim. As the *In re Angstadt* court states the disclosure does not have to provide examples of all species within appellants' claims where it is within the skill of the art to make them. There is no evidence to the contrary.

The examiner states "[t]he appellants argue that their own examples do not support the determination of non-enabling scope of the invention. Nevertheless, the record is viewed as a whole. If the applicants could not show superconductivity with a $T_c > 26^\circ\text{K}$ for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made." The examiner avoids the essential issues. Even though appellants' claims do not cover inoperable species, *In re Angstadt* clearly permits a claim to include

inoperable species where to determine which species works does not require undue experimentation. The examiner has not presented any substantial evidence that undue experimentation is required to practice appellants' claim. This is the examiner's burden. On the other hand, appellants have presented five affidavits of experts, the book of Poole and the article of Rao all of which agree that once a person of skill in the art knows of appellants' invention, it is straight forward to fabricate other sample. Also, in response to the examiner's inquiry, "if the applicants could not show superconductivity with a $T_c > 26^\circ\text{K}$ for certain compositions falling within the scope of the present claims, it is unclear how someone else skilled in the art would have been enabled to do so at the time the invention was made", it is clear that a person of skill in the art would have been enabled by routine experimentation following applicants teaching to determine other samples with $T_c > 26^\circ\text{K}$. This is all that is required, and there is no evidence in the record to the contrary.

In the prosecution and the brief, appellants have noted that the examiner has taken a contrary view to appellants' five affiants each of whom has qualified himself as an expert in the field of ceramic technology and in superconductivity. Also, the examiners' argument for nonenablement is primarily based on the examiner "**deeming**" the rejected claims nonenabled based in the unsupported assertion that the art of high T_c is unpredictable and not theoretically understood, that is, the examiner's opinion or belief that the claims are not enabled. In the prosecution and the brief appellants requested the examiner to

submit an affidavit to qualify himself as an expert to conclusorily "**deem**" the rejected claims nonenable and to substantiate the unsupported assertions. The examiner has not submitted an affidavit. The examiner's opinions should therefore be stricken from the record. 37 CFR 104(d)(2) states "[w]hen a rejection in an application is based on facts within the personal knowledge of an employee of the office ... the reference must be supported when called for by the applicants, by an affidavit of such employee." (Emphasis Added)

The examiner further states:

The appellants argue that the "Examiner has provided no substantial evidence to support this assertion (of non-enabling scope of the invention). It is respectfully requested that the Examiner support (his) assertion with factual evidence and not unsupported statements." Nevertheless, the determination of non-enabling scope is maintained for the reasons of record.

Appellants note the examiner has not responded to appellant request that the examiner support his view on nonenablement with an affidavit of facts rather than unqualified conclusory statements.

The examiner further states:

The appellants argue that the "standard of enablement for a method of use is not the same as the standard of enablement for a composition of matter" and that their claimed invention is enabling because it is directed to a method of use rather than a composition. Basis is not seen for that argument, to the extent that it is understood.

Applicants discovered that metal oxides had $T_c > 26^\circ\text{K}$. This was not known prior to applicants' discovery. Once this is realized, the only enablement required for appellants' claims are to cool a metal oxide below the T_c and to provide a superconducting current. It is not necessary for applicants to provide a detailed method of making every composition which can be used within the scope of their claims. Applicants' claims are not directed to the composition of matter. They are directed only to the use of the metal oxide as a superconductor with a $T_c > 26^\circ\text{K}$, that is, as a circuit element in operation. It was within the skill of the art to fabricate metal oxides using the appellants teaching and test them for a $T_c > 26^\circ\text{K}$ using techniques well known prior to appellants filing date.

Appellants agree that process of use claims are subject to the statutory provisions of 35 U.S.C. 112, first paragraph. However, those provisions are directed to the claimed process of use invention and not to a composition of matter claim. It is not relevant how a composition, which can be used to practice appellants' claims, is made since the invention is how the composition is used.

Thus the type of enablement is different. For example, if a circuit containing a resistor is claimed, the applicant does not have to teach all known methods to fabricate the resistor and the claim will read on circuits including resistors made by methods discovered after the filing date of the application. Here appellants are claiming a high T_c superconductor (a type of resistor) that carries a current below a temperature of $T_c > 26^\circ\text{K}$. This is a circuit element in operation.

The appellants asserted in the brief and in the prosecution that the examiner has not shown by evidence not contained within appellants' teaching that the art of high T_c superconductors is unpredictable. In response the examiner states "[t]o the extent that the same assertion is understood, the rejection is maintained for the reasons of record." Applicants' statement is very clear. The examiner is trying to avoid the issue since examiner has not shown by evidence not contained within applicants' teaching that the art of high T_c superconductors is unpredictable. The examiner has merely "**deemed**" it to be so.

Appellants have extensively referred to "Copper Oxide Superconductors" by Charles P. Poole, Jr., et al., (hereinafter, "the Poole book" or "the Poole article") as supporting their position that higher temperature superconductors were not that difficult to make after their original discovery. This is because methods of making metal oxides which could be used to practice appellants' claimed invention were well known prior to applicants discovery that metal

oxides had a $T_c > 26^\circ\text{K}$. In response the examiner states "Initially, however, it should be noted that the Poole article was published after the priority date presently claimed". It is not relevant that the Poole article was published after the priority date since it is clear evidence that only routine experimentation was needed to practice appellants' claimed invention and there is no indication that anything more than appellants' teaching is needed. The examiner further comments on the Poole book stating, "[a]s such, it does not provide evidence of the state of the art at the time the presently claimed invention was made". As noted in the brief, Poole clearly states that the materials that can be used within the scope of applicants claims were easily made. And as stated above the examiner has acknowledged that the fabrication techniques were well known prior to appellants' invention. Poole states that is why so much work was done in so short a period of time. This is clear and convincing evidence that persons of skill in the art were fully enabled by applicants teaching to practice applicants' claimed invention. It is not necessary for appellants to show that the data was generated prior to appellants' filing date. The examiner has not stated, nor is there any evidence presented by the examiner, nor is there any indication in the Poole book that anything more than what appellants taught was necessary to practice appellants' claimed invention. It is only necessary that persons of skill in the art can practice applicants claimed invention from appellants' teaching without undue experimentation. As stated in *In re Angstadt* there is no requirement of no experimentation to practice the claimed invention which is the standard the examiner is apparently applying.

The examiner further states:

Moreover, the present claims are directed to processes of using metal oxide superconductors, not processes of making them. Even if the Poole article provided direct evidence of the state of the art at the time the invention was made, which it apparently does not, that evidence still does not pertain to the issue at hand, namely, the process of using metal oxide superconductors to conduct electricity under superconducting conditions.

The Poole article clearly does not pertain to the process of using metal oxide superconductors to conduct electricity under superconducting conditions prior to appellants' invention since this is appellants' discovery and their invention. The Poole article clearly shows that once appellants revealed their discovery, it was easy to practice appellants' invention and to fabricate other materials to practice appellants' claimed invention. It is not relevant that the Poole article is after the date of appellants' patent application since there is no indication in Poole that anything more than what appellants have taught was used to create the easily created high T_c materials referred to by Poole. The Poole article clearly shows how these easily made materials can be used to practice appellants' claimed invention. The Poole book is directed to metal oxide materials carrying a superconducting current at $T_c > 26^\circ\text{K}$ which can be

used in a variety of circuit configurations. Chapter 10 pp . 196-218 of the Poole book is directed to the process of using metal oxide superconductors to conduct electricity under superconducting conditions. The first paragraph of Chapter 10 states:

The principal applications of superconductors are based upon their ability to carry electric current without any loss, and therefore it is important to understand their transport properties. This chapter begins with a discussion of resistivity and critical current flow in the absence of externally applied fields. This is followed by a discussion of several techniques involving applied fields and thermal effects. The chapter concludes with sections on tunneling and the Josephson effect.

Applicants acknowledge the Preface of the Poole Article states in part at A3:" The field of high-temperature superconductivity is still evolving ..." And applicants agree with the examiner that "the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published." The automobile was discovered prior to 1900 and that field still , more than 100 years latter, continues to grow. The inventor of the automobile would have been able to claim an "automatically moving carriage under the power of an engine " which would be dominant to every automobile manufacture today even through the automobile

technology of today was unknown 100 years ago. Notwithstanding such a dominant claim, others could invent more specific improvements as the field continued to grow, on the basis of on-going basic research. That the field of high-temperature superconductivity continued to grow, on the basis of on-going basic research, after the Bednorz and Meuller article was published does not mean that appellants are not entitled to a claim to their discovery even though it may dominate the inventions of others based on subsequent on-going basis research where that ongoing basis research followed appellants' teaching to fabricate, as taught by appellants, other specific materials to use as taught by appellants.

In the first two full paragraphs on page 20 of the answer the examiner incorrectly refers to three affidavits submitted by appellants. Appellants have submitted five affidavits all of which, as noted above, have been considered and entered. The affidavits of Shaw and Duncombe cited numerous text and articles in support of their affidavits. The affidavit of Duncombe provides several hundred pages of experimental data in regards to fabrication of numerous examples of metal oxides to practice appellants' claimed invention.

Appellants disagree that they have only enabled compositions containing an alkaline earth element and a rare earth or Group IIIB element to result in superconductive compounds which may in turn be utilized in the instantly claimed methods. This new ground for rejection necessitates the introduction of

new evidence to show why the examiners statement is incorrect. As noted above, there are numerous examples of high Tc superconductors made using the general principals of ceramic science as taught by appellants that existed prior to appellants' earliest filing date. Some of that data is in the affidavit of Duncombe, the Poole book and the Rao article.

In regards to the affidavits of Tsui, Dinger and Mitzi the examiner states "However, that additional indication also is considered to be a conclusory statement unsupported by particular evidence." To the extent that this statement is true the affidavits of Shaw and Duncombe, the book by Poole and the article by Rao provide particular evidence. In the answer even though these affidavits and the book by Poole have been considered, the examiner has not commented on this particular evidence and the examiner has not stated that this particular evidence does not support appellants' view that their claims are fully enabled.

The examiner restates what is stated in the affidavits and comments:

It is the examiner's maintained position that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known. The affidavits are not effective to demonstrate enablement at the time the invention was

made. As stated in paper #66, page 8, one may now know of a material that superconducts at more than 26K, but the affidavits do not establish the existence of that knowledge on the filing date of the present application.

The examiner states: " The affidavits are not effective to demonstrate enablement at the time of the invention was made". Appellants disagree that applicants five affidavits do not demonstrate enablement at the time the invention was made. The affidavits clearly state that the knowledge that existed prior to applicants filing date permitted a person of skill in the art to practice appellants' invention as claimed without undue experimentation. The examiner has presented no evidence to the contrary.

It is not necessary for applicants to provide experimental evidence for all materials that come within the scope of applicants' claims. It is only necessary that a person of skill in the art can practice applicants' claimed invention without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. It is the examiner's burden to show that undue experimentation is required. The examiner has not done this. Also, that there may be specific metal oxides having high T_c , which are not specifically identified in appellants' specification does not mean that appellants are not entitled to a claim generic to such a species where that species can be made without undue experimentation following appellants' teaching. In re Robins 166 USPQ 552,

555, CCPA 1970, Representative samples are not required by the statute and are not an end in themselves. The examiner has not shown that a person of skill in the art must exercise undue experimentation to make such a species. Thus the examiner has failed to meet his burden.

The examiner concedes that "that while general principles of ceramic fabrication were most certainly known prior to the filing date of the instant application, the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known." The examiner has acknowledged that techniques to fabricate materials for use within the scope of applicants' claims were known prior to appellants' invention. Appellants agree that "the utilization of such techniques to produce superconductive materials within the scope of the instant claims were not known," since this was appellants' invention. If "the utilization of such techniques to produce superconductive materials within the scope of the instant claims" were known prior to applicants invention, applicants would not be the inventor. Prior to applicants discovery persons of skill in the art would not make metal oxides to use as a high T_c superconductor since such use had to await appellants' discovery. Such fabrication techniques have been used to produce metal oxides for use for some other purpose.

The affidavit of Leonard submitted December 15, 1998 shows that 5,689 articles reference appellants' article. The examiner apparently wants to limit

appellants' claims to their specific embodiments when the record as a whole clearly shows that all known high Tc materials can be made according to appellants' teaching. If the appellants are limited, as the examiner would have them limited, they should not have revealed their discovery and instead spent the rest of their life, in secret, experimenting to generate these 5,689 experimental efforts, according to their original teaching, so that they could get generic claims to their original discovery.

For the reasons given above and in the brief appellants request the board to reverse the examiner's rejection of claims under 35 USC 112, first paragraph.

35 USC 112, Second Paragraph Rejections

With respect to the remaining claims rejected under 35 U.S.C. 112, second paragraph, the examiner has not rebutted appellant's remarks appearing at pages 102-113 of the Substitute Brief. In response to appellants' arguments that the terms "rare-earth like", " perovskite-like", "layer-type" and "perovskite-type" are definite, the examiner states "those arguments are not found to be persuasive," but the examiner gives no reasons for this view.

At page 21 of the answer, the examiner comments in regard to the claims rejected under 35 UCS 112, second paragraph, the examiner states that "[n]ote the Examiner declines to comment on appellants remarks regarding the

after-final submissions which have not been entered or considered by the examiner." These unentered after final submissions provide evidence that the terminology "perovskite-like", "perovskite-type", and "rare-earth-like" were understood by persons of skill in the art prior to appellants' filing date. This evidence is in addition to evidence previously submitted to show that these terms were well understood in the art. Thus this new evidence is not directed to any new issues but is additional evidence on the same issue. Prior to the Final Action the undersigned attorney requested the examiner to specify what information was needed to convince the examiner that these terms were well understood in the art. The examiner did not provide any guidance to appellants. Thus a trial and error approach was used to see if what was submitted was sufficient to convince the examiner. The examiner again in the Final Action indicated he was not convinced and appellants submitted additional evidence in the after final submissions. Some of the additional evidence is issued US patents having claims containing the identical terminology which the examiner finds indefinite. Other evidence is issued US patents using similar terminology in issued claims indicates that the use of such terminology in US patent claims is standard USPTO practice.

The examiner states:

Each patent application is considered on its own merits. In some contexts it may have been clear in the art to use the term "like",

such as when the "like" term is sufficiently defined. In the present case, however, the terms "rare-earth like" and " perovskite-like" are unclear.

The examiner would not comment on the after final submissions which bring to the attention of the examiner standard patent office practice which the patent examiner should know. There are many issued patents having claims including terminology "-type", "-like" and similar combination terms. The examiner's refusal to give reasons for rejecting applicants' use of this terminology while there are many issued patents using this terminology in the claims is "arbitrary and capricious". The examiner must give reasons. It is not sufficient to say "Each patent application is considered on its own merits" without giving reasons as to what the merits are in the present application which render these terms indefinite while not indefinite in the claims of issued patents.

Appellant's published their publication in Z. Phys. B - Condensed Matter 64 (1986) 189-193 (Sept. 1986) which is incorporated by reference in the present specification at page 6, lines 7-10. (This article is referred to here in as a appellants' article.) Appellants filed the first application in the lineage for the present application on May 22, 1987. To the extent that the terminology "perovskite-type", "perovskite-like", etc. were not known prior to applicants' discovery, it was placed into the vernacular of persons of skill in the art in the approximately eight months between the publication of appellants' article the

earliest filing date of the present application . Appellants' article was published in a highly regarded physics journal. The referees for the article apparently understood what appellants meant by this terminology. The appellants were awarded a Nobel Prize based on this article. The Nobel committee apparently understood what appellants were referring to. Appellants' article at page 189, fourth line of the abstract, refers to "a perovskite-like mixed-valent copper compound"; at page 189, lines 14-15 of the right column, refers to "perovskite-type or related metallic oxides"; at page 192, line 12 of the left column, refers to "layer-like phases"; and the 8th line of the conclusion at page 192 refers to "a metallic perovskite-type layer-like structure". As stated in the brief at pages 106-107 the book by Poole uses this terminology attributing it to applicants article. Chapter VI, Section D, of the Poole Book is entitled "Pervoskite-type Superconducting Structures" pp. 78-81. It is thus clear that the objected to terminology is understood by persons of skill in the art as of the earliest filing date of the present application. Moreover, as shown in the brief 102 issued United States Patents uses the terminology "pervoskite like", two of which use this term in the claims. It is thus accepted USPTO practice to accept this term as definite. Also, as shown in the brief there are many issued patents using combinations of "-type" and "-like" with claims. Thus it is accepted USPTO practice to accept such terminology as definite.

Moreover, in the brief at pages 7-20, appellants extensively discuss the terminology of the present application which incorporates by reference appellants' article.

Moreover, the affidavits of Duncombe and Shaw refer to a number of articles and texts on the general principles of ceramic science. One of these texts is "Structures, Properties and Preparation of Perovskite-type Compounds", F. S. Galasso (1969). This book was published about eighteen years before appellants' filing date. A copy of the complete text of this book was provided with the affidavits. The examiner does not comment on why a person of skill in the art would not know what a perovskite-type compound was in view of this book and the teaching of applicants' article.

At page 105 of the brief appellants note that in Attachment A of their response of December 11, 1998, there are listed 68 United States Patents using the terminology "rare earth like" or rare earth and the like" and in Attachment B of this response there are listed 4 United States Patents with the term "rare earth like" or similar term in the claims. The examiner has not commented on why this term is not understood by a person of skill in the art in view of the use of this term in the specification and claims of issued United States Patents. In the brief appellants refer to numerous articles using the terminology "rare-earth-like" published before appellants filing date. The examiner has not commented on this. Appellants explain the meaning of "rare-earth-like" at page 7, lines 8-25,

“[a] rare earth-like element (sometimes termed a near rare earth element) is one whose properties make it essentially a rare earth element ...”.

It is thus clear that the meaning of “perovskite-type”, “perovskite-like” and “rare-earth-like” are apparent from applicants teaching and the prior art, and that it is accepted USPTO practice to use such terminology in the claims. The examiner has not commented on nor rebutted appellants arguments. The examiner has merely stated that there terms are indefinite without further comment.

For reasons given above and in the brief, appellants request the Board to reverse the examiners rejection of claims under 35 USC 112, second paragraph.

CONCLUSION

In view of the argument herein and in the brief, Applicants request the Board:

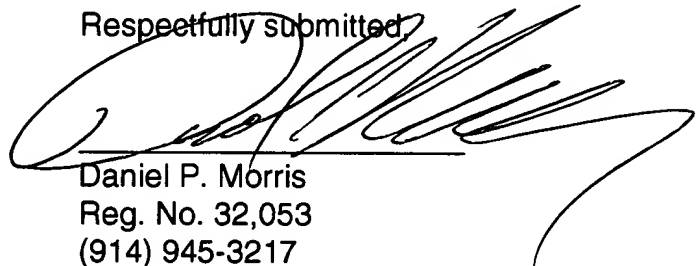
1. reverse the determination that claims 24-26, 86-90, 96-135 and 137-177 are not supported by the priority document;
3. reverse the rejection of claims 24-26, 88-90, 96-102, 109-113, 129-131, 134, 135, 139-142, 145, 149-151, 158, 159, 164-166, 169-170 and 174-177 as not enabled under 35 USC 112, first paragraph; and



4. reverse the rejection of claims 86, 87, 96, 108, 112, 113, 117, 118, 122, 123, 127, 128 and 147 indefinite under 35 USC 112 second paragraph.

Please charge any fee necessary to enter this paper to deposit account 09-0468.

Respectfully submitted,



Daniel P. Morris
Reg. No. 32,053
(914) 945-3217

IBM CORPORATION
Intellectual Property Law Dept.
P.O. Box 218
Yorktown Heights, New York 10598

RECEIVED
JUL 21 2000
TC 1700 MAIL ROOM

Attachment A

THEORY OF SUPERCONDUCTIVITY

By

M. von LAUE

Kaiser-Wilhelm-Institut für physikalische und Elektro-Chemie
Berlin—Dahlem

Translated by

LOTHAR MEYER

University of Chicago, Chicago, Illinois

and

WILLIAM BAND

The State College of Washington, Pullman, Washington



ACADEMIC PRESS INC., PUBLISHERS

New York, 1952

Preface

The aim of this book is to bring our picture of superconductivity into sharper focus by extending Maxwell's electrodynamics along lines first suggested in 1935 by Fritz and Heinz London. This extension will be carried just so far as it succeeds in accounting for known facts, and the reader will see for himself how extensive an area this covers. Beyond this, still exist a number of unexplained facts, which will be ignored. We recall that Clerk Maxwell's electromagnetic theory at first ignored the well known dispersion of the refractive index and that Heinrich Hertz's theory of the electrodynamics of moving bodies ignored the Fresnel drag phenomenon; also, early thermodynamics and gas theory were based on the simple equation of state $PV = RT$, although it was known that no actual gas obeyed this equation exactly. After all, theory can approach the truth only by successive approximations.

We have a suspicion that experimental evidence has been insufficient to establish many of these unexplained observations. The ideal solid body, for instance, is a single crystal; but most experiments on superconductivity have been performed with polycrystalline materials, whereas even the best obtainable single crystals, if of useful size, are mosaics of small crystals at whose boundaries the lattice is discontinuous. Hysteresis phenomena are nearly always observed in the transitions between normal states and superconducting states; but we know that at low temperatures, particularly in solid bodies, other relaxation effects may also arise that would completely obscure the theoretical equilibrium between two phases.

Finally many of the unexplained observations have been encountered only a few times, perhaps only once, so that confirmation under varied conditions seems necessary before we are unduly concerned about them.

The phenomenon of superconductivity was discovered in 1911. In spite of this fact, the subject is still only in its initial stages. Should the present theory prove to be true, it will have accomplished for the superconductor what the original Maxwell theory did for the normal conductor and the nonconductor. It does not aim to do more.

In none of its different forms does the atomic theory of superconductivity seem to us to be so far developed that we would wish to include it in this book. It is, however, fairly certain that the persistent current in a superconducting ring is the analog to the atomic persistent currents assumed by the Bohr model to be present inside atoms and molecules. In both cases we are dealing with typical quantum effects which remained unintelligible in classical physics. It seems to me that the main interest for physics in the study of superconductivity lies precisely in this unequivocal experimental proof of the existence of such quantum currents. In any case this book will show how these currents can be fitted into the Maxwell theory.

All Rights Reserved

No part of this book may be reproduced in any form, by photostat, microfilm, or any other means, without written permission from the publishers.

TRANSLATION COMPLETED 1949

Library of Congress Catalog Card Number: 52—7310

Recently the first volume of Superfluids by Fritz London was published. His book has partly the same aim as ours, but often uses a different approach. Our *Theory of Superconductivity* actually goes further by including tensor and non-linear generalizations of the theory. There are certain indications that such generalizations are necessary although the final decision depends on future experiments. I believe that this presentation of the theory may serve at least as a stimulus for these experiments: such a suggestion was made by J. Geiss, *Ann. d. Phys.* (6), 9, 40, 1951.

MAX von LAUE

December, 1951

Table of Contents

PREFACE	Page
SYMBOLS	v
CHAPTER	viii
1. Fundamental Facts	1
2. Current Distribution between Superconductors in Parallel	8
3. Fundamental Equations of the Maxwell-London Theory	12
4. Space Charges in Superconductors	19
5. The Conservation of Energy	20
6. The Telegrapher's Equation for Superconductors with Cubic Crystal Structure	22
7. Stationary Fields	24
8. The Current Flowing in a Wire	35
9. The Current Flowing in a Hollow Cylinder	44
10. The Cylinder in a Homogeneous Magnetic Field	48
11. The Sphere in a Homogeneous Magnetic Field	55
12. Persistent Currents	61
13. The Maxwell and London Stresses	75
14. The Electrodynamic Potential	84
15. Electric Waves in Superconductors with Cubic Crystal Structure	91
16. The High-Frequency Resistance of Superconductors	94
17. Thermodynamics of the Transition between Normal and Superconducting Phases	103
18. The Critical Magnetic Field for Thin Superconductors	112
19. The Intermediate State	119
20. A Nonlinear Extension of the Theory.	126
APPENDIX	137
INDEX	139

SYMBOLS

A	vector potential
a_p	undetermined constants, $p = 1, 2, \dots$
a	a numerical ratio
a_p	undetermined constants, $p = 1, 2, \dots$
B	magnetic induction
β	reciprocal penetration depth
c	velocity of light
C_m	closed curves $m = 1, 2, \dots$
c_N, c_S	specific heats per mol of normal and superconducting phases
κ	an undetermined multiplier
D	electric displacement
d	distance
δA	work done in virtual displacement
∂A	work done in material displacement
δF	change in free energy in virtual displacement
δn	virtual displacement of a surface element
$d\sigma$	surface element
ds	line element
$d\tau$	volume element
∂u	material displacement
∂V	potential energy change due to material displacement
E	electric field intensity
E_a	electric field components, $a = 1, 2, 3$
E	total energy
E_0	amplitude of E waves
$[\mathbf{E} \times \mathbf{H}]$	vector product of E and H
ϵ	dielectric constant
F	free energy
f_N, f_S	free energy per mol of normal and superconducting phases
F^*	force per unit area due to Maxwell stresses
F^*	free energy of supercurrent
G	electromagnetic momentum associated with the supercurrent
G_a	components of G, $a = 1, 2, 3$
γ	a numerical factor
H	magnetic field intensity vector
H_a	components of H, $a = 1, 2, 3$

H^0	external homogeneous magnetic field
H_c	critical magnetic field
H_i, H_e	internal and external values of H
$H_0(x)$	Hankel's function of x , first kind zero order
$H_1(x)$	Hankel's function of x , first kind first order
I	electric current in a line or current in a surface
i	electric current density vector
i_a	components of i, $a = 1, 2, 3$
i_1, i_2, i_3	i_1, i_2, i_3 , components of i, cartesian or polar
i_0	ohmic current density vector
i^*	supercurrent density vector
i_m	maximum current density vector
i_n	current density normal to a given surface element
i^*	surface density of current
$(i^* \cdot G)$	scalar product of i^* and G
i	square root of minus one
$I_n(x)$	Bessel functions, $n = 0, 1, 2$
k	complex wave number
k_n	complex wave number for normal conductor
K_n or K_s	total force on a surface element due to electromagnetic stress
K	force per unit volume in matter due to Maxwell-London stresses
L	a length
λ	superconductivity constant
$\lambda_{\alpha\beta}$	superconductivity tensor $\alpha, \beta = 1, 2, 3$
M	intensity of permanent magnetisation
μ	magnetic permeability
N	number of superconducting electrons per cubic centimeter
n	unit normal vector
n_1, n_e	unit normal vector directed inwards or outwards
ν	frequency (numerical)
P	force on surface due to London stresses
$p_{\alpha\beta}$	coefficients of induction $\alpha, \beta = 1, 2, \dots$
p^{ss}	self-induction for superconductors
p^{sc}	mutual induction between super- and normal conductor
φ	azimuthal angle
φ	imaginary part of a complex function
Φ	electrostatic or magnetostatic potential
ψ	real part of a complex function
Ψ	superconduction scalar potential
Q	quantity of heat
Q	cross cut in n -ply connected region
Q	rate of flow of energy in radiation field

R_c real part of complex function
 R a radius
 R_i, R_e internal and external radii
 r, θ, φ polar coordinates
 ρ charge density
 ρ^0 charge density for ohmic current carriers
 ρ^s charge density for supercurrent carriers

s_N, s_S

S entropy per mol in normal and superconducting phases
 S_C linear dimensions of a surface
 S_C „period“ of a multiple valued function on a curve C
 σ equal to the flux of induction thru the loop C
 σ electric conductivity
 $\sigma_{\omega\beta}$ electric conductivity tensor $\alpha, \beta = 1, 2, 3$

T temperature in $^{\circ}\text{K}$

T_s transition temperature for superconductivity

$T(\mathbf{E})$ Maxwell stress tensor

$T(\mathbf{H})$ Maxwell stress tensor

t time

τ_a numerical constants $a = 1, 2, \dots$

θ latitude angle

θ_N, θ_S Debye temperatures for normal and superconducting phases
 $\Theta_{\omega\beta}$ The London stress tensor in superconductor $\alpha, \beta = 1, 2, 3$

U total energy of the field

U real part of complex function W

u a general function of position and time

V volume or potential

V imaginary part of complex function W
 V electromotive force

W resistance

W a complex function

ω angular frequency

$W()$ differential operator for the telegrapher's equation

x, y, z cartesian coordinates

x_1, x_2, x_3 cartesian coordinates

χ permeability

χ a function in the complex plane

Z complex impedance

ζ a function in the complex plane

ζ a variable of integration

CHAPTER 1

Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.¹ He was the first to liquefy helium and so to produce temperatures below 10°K . With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about 4.2°K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal far below even 1°K . Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as 20°K . However, among these latter substances hysteresis phenomena mentioned in the „Introduction“ are so much more strongly evident that in testing the present theory we prefer to employ only the „good“ superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature T_s . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

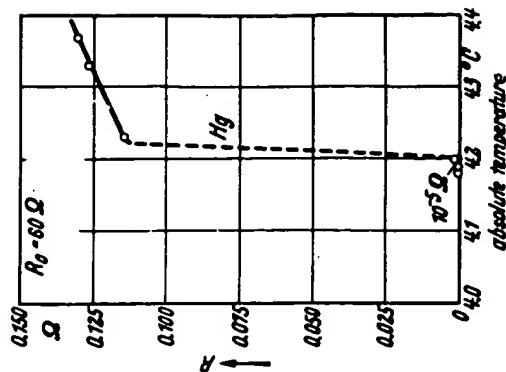


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance R ; R_0 , the resistance of solid mercury extrapolated to 0°C , is 60 ohms.

¹H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

the d-c resistance becomes unmeasurably small represents the true transition point. Because of this uncertainty Table 1-1 quotes the transition points only to one-tenth of a degree.

Table 1-1

Superconducting Elements

Name	Atomic Number	Transition Temperature	Crystallographic System	Crystal Class*
Aluminum	13	1.2 °K	Cubic	O_h and D_{6h}
Titanium	22	0.5 °K	Cubic and hexagonal	O_h and D_{6h}
Vanadium	23	4.3 °K	Cubic	O_h
Zinc	30	0.9 °K	Hexagonal	D_{6h}
Gallium	31	1.1 °K	Rhombohedral	V_h
Zirconium	40	0.7 °K	Cubic and hexagonal	O_h and D_{6h}
Niobium	41	9.2 °K	Cubic	O_h
Cadmium	48	0.6 °K	Hexagonal	D_{6h}
Indium	49	3.4 °K	Tetragonal	D_{4h}
Tin	50	3.7 °K	Tetragonal†	D_{4h}
Lanthanum	57	4.7 °K	Cubic and hexagonal	O_h and D_{6h}
Hafnium	72	0.3 °K	Hexagonal	D_{6h}
Tantalum	73	4.4 °K	Cubic	O_h
Rhenium	75	0.9 °K	Hexagonal	D_{6h}
Mercury	80	4.2 °K	Rhombohedral	D_{3d}
Thallium	81	2.4 °K	Cubic and hexagonal	O_h and D_{6h}
Lead	82	1.2 °K	Cubic	O_h
Thorium	90	1.4 °K	Cubic	O_h
Uranium	92	0.8 °K	Rhombohedral	V_h

* The atomic structure does not change during the transition from normal conductor to superconductor therefore the crystal class does not change either. The glasses are defined according to Schoenflies.

† Besides the tetragonal white tin there exists a gray modification with a crystal structure of the diamond type which, however, does not become superconducting.

In order to obtain curves such as in Fig. 1-1, the resistance is calculated from the potential drop along a wire carrying a current. For this purpose separate potential leads are soldered to the ends of the wire, in addition to the leads for the current, and are connected to a highly sensitive potentiometer. But if one merely wishes to verify the complete disappearance of the resistance below the transition temperature T_s , experiments with persistent currents, also due to Kamerlingh-Onnes,² are far more convincing and exact.

(b) One possible procedure is to place a ring or short-circuited coil in a magnetic field while its temperature is still above T_s , cool it down until superconductivity appears, and then remove it from the field. The induced

²H. Kamerlingh-Onnes, *Commun. Leiden*, 140b, 141b, (1914).

electromotive force produces a current in the superconductor which will persist indefinitely unchanged in magnitude as long as superconductivity remains. The ring forms an ideal permanent magnet, and, when placed in an external homogeneous magnetic field, it experiences a torque corresponding to its magnetic moment. Two rings with persistent currents attract or repel each other, depending on their relative orientations, just as for ordinary currents, except that no emf's are needed to maintain them. It does not matter whether the rings are homogeneous or consist of several different superconductors, or whether their temperature is constant in space or time; it is only necessary that no part of the ring shall leave the superconducting state.³ Should this occur, the current is quenched almost instantaneously. For example, a ring carrying a persistent current may be cut at some point across which a galvanometer has been connected through normally conducting leads. Before the cut is made, the galvanometer will register zero current; but at the instant that the ring is broken, it will show a short current impulse. The energy of the persistent current, for the most part magnetic energy, is then transformed into Joule heat in the normally conducting wires.

A necessary condition for the existence of any persistent current is that the superconductor form a doubly connected body or, briefly, a ring, or more generally a multiply connected body. No persistent currents can exist in a simply connected body such as a sphere. Results that apparently contradict this arise because only parts of the specimen, among them doubly or multiply connected parts, may become superconducting, while the rest of the specimen remains either normal or in the intermediate state (see Chap. 12 (g) and 19). An electromagnet using the persistent current has been described by E. Justi.⁴

(c) In contrast to the normal current, which we shall call the ohmic current, the superconducting current (or supercurrent) does not penetrate very far into the specimen. It has been known for a long time that the superconductivity of thin tin films on copper or some other normally conducting metal, even down to a thickness of only 10^{-4} cm, does not differ from the superconductivity of thick tin wires. The contradictory evidence found by Burton⁵ using somewhat thinner films is outweighed by the observations of Shalnikov⁶ and by those of Appleyard and Misener⁷ using lead, tin, and mercury films as thin as 5×10^{-7} cm. These workers found practically the same transition temperatures as in the bulk metals, the small differences observed being within the experimental error.

The first quantitative estimates of the penetration depth of the supercurrent and its associated magnetic field derived from observational evidence,

³It is fairly certain that temperature fluctuations have no effect because no investigator has ever mentioned any such effect.

⁴E. Justi, *Elektrotech. Z.*, 63, 577 (1942).

⁵E. F. Burton, *Nature*, 138, 459 (1934).

⁶A. Shalnikov, *Nature*, 142, 74 (1938).

⁷T. S. Appleyard and A. D. Misener, *Nature*, 142, 474 (1938).

were made by the author⁸ from the experimental results of Pontius using lead wires⁹ (Fig. 18-1). Appleyard, Bristow, and H. London¹⁰ and a year later Shoenberg¹¹ found the same order of magnitude, namely 10⁻⁵ cm, using films and spherical drops of mercury. This holds for temperatures within a few tenths of a degree below the transition temperature T_s . However, if we are within one-tenth of a degree of T_s , according to the above work of Shoenberg, the penetration depth increases suddenly and appears to become infinitely great at the transition point (see Fig. 11-3). This means that in a certain sense the electrical properties of the superconductor change continuously into those of the normal conductor. The measurements by McLennan, Burton, Pitt and Wilhelm¹² and H. London¹³ on the high-frequency resistance of superconductors also fit in with this concept: the resistance to rapid oscillations showed no discontinuity at the transition point, but joined smoothly at T_s with that of the high-frequency resistance of the normal conductor (Fig. 16-2).

(d) The transition from normal to superconductor does not change the form or the volume of the specimen; its lattice remains the same not only in its symmetry but also in its three lattice constants. This was proved for lead by Kamerlingh-Onnes and Keesom using x-ray analysis.¹⁴ The coefficient of thermal expansion (which incidentally is very small) does not change at the transition. Of special significance is the optical identity of the two phases, because in normal conductors the optical constants are intimately related to the electrical conductivity. The observations of Daunt, Keely, and Mendelsohn,¹⁵ of Hirschlaff,¹⁶ and of Hilsch¹⁷ revealed no difference in the appearance of the metal. One cannot tell by visual observation whether the metal is normal or superconducting.

(e) The relation between superconductivity and magnetic field is of the highest significance. The first steps toward disclosing this relation were made in 1913 by Kamerlingh-Onnes¹⁸ who noticed that at each temperature there existed a critical value H_c of the magnetic field that would destroy the superconductivity. We can obtain the simplest and clearest results by putting a wire in a longitudinal magnetic field, i. e.,

⁸M. v. Laue, *Ann. Physik*, **82**, 71, 253 (1938).

⁹R. B. Pontius, *Nature*, **189**, 1065 (1937).

¹⁰T. S. Appleyard, T. R. Bristow, and H. London, *Nature*, **148**, 433 (1939).

¹¹D. Shoenberg, *Nature*, **148**, 434 (1939).

E. Laurmann and D. Shoenberg, *Nature*, **180**, 747 (1948).

¹²C. McLennan, A. C. Burton, A. Pitt, and J. O. Wilhelm, *Proc. Roy. Soc. (London)*, **186**, 52 (1932); **188**, 245 (1934).

¹³H. London, *Proc. Roy. Soc. (London)*, **176**, 522 (1940).

¹⁴W. H. Keesom and H. Kamerlingh-Onnes, *Commun. Leiden*, **174b** (1924).

¹⁵J. G. Daunt, T. C. Keely, and K. Mendelsohn, *Phil. Mag.*, **28**, 264 (1937).

¹⁶E. Hirschlaff, *Proc. Cambridge Phil. Soc.*, **88**, 140 (1937).

¹⁷R. Hilsch, *Physik. Z.*, **40**, 592 (1939).

¹⁸H. Kamerlingh-Onnes, *Commun. Leiden Supplement* **85** (1913).

parallel to the axis of the wire. The dependence of the a-c resistance on the magnetic field H for this case is shown in Fig. 1-2, while Fig. 1-3 shows the critical value of the magnetic field as a function of temperature for several metals.

Figure 1-4 shows an extrapolation of these curves down to the absolute zero of temperature according to a relation that is empirically confirmed in some cases:

$$H_c = a(T_s^2 - T^2)$$

At $T = 0$ the tangent of this curve is horizontal, as thermodynamics demands (Chap. 17). The maximum values of H_c

at $T = 0$ lie between 100 and 1000 oersteds for pure metals and may be much higher for alloys and compounds.

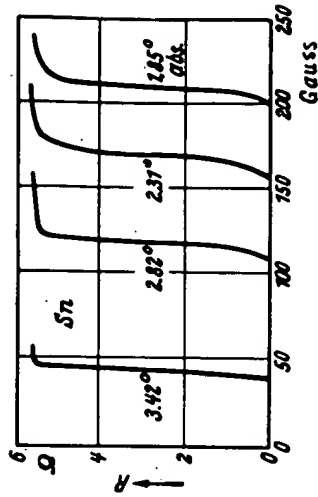


Fig. 1-2. Transition to superconductivity in a longitudinal magnetic field for tin at different temperatures. (After Steiner and Grassmann, *Supraleitung*. Braunschweig, 1937.)

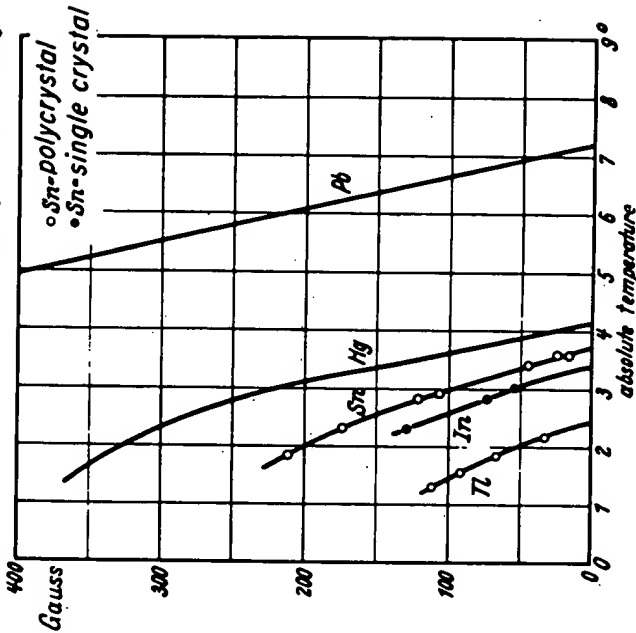


Fig. 1-3. Critical value of the magnetic field H_c as a function of temperature for different metals. (After Steiner and Grassmann, *Supraleitung*. Braunschweig, 1937.)

A current I produces at the surface of a straight wire of radius R a magnetic field H :

$$H = \frac{I}{2\pi c R} \quad (1-1)$$

in Lorentz units, which we shall generally employ.¹⁹ We should therefore expect to find a critical value I_c of the current which would destroy superconductivity, and this has been confirmed by observation. According to eq. (1-1) the relation between I_c and H_c ought to be

$$I_c = 2\pi c R H_c \quad (1-2)$$

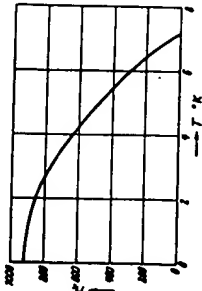


Fig. 1—4. Critical value of the magnetic field H_c as a function of temperature for lead (approximate curve).

essentially on this equation. It is to be hoped that experimental work will soon be able to remove this uncertainty.

(f) The earliest theory of superconductivity visualized the superconductor as simply a conductor with zero resistance. But on the Maxwell theory this assumption would have an important consequence; the interior of a perfect conductor would be completely shut off electromagnetically from any outside influence. If such a conductor were placed in a static magnetic field its interior would remain field free, the lines of force, or rather of induction, would diverge in front and converge behind as if going round a body of zero permeability (Fig. 1-5). But the result would be different were one to put the specimen in an external field while it was still above the transition temperature T_c , and then cool it in the field until the resistance disappeared. Above T_c the lines of force would go through the metal without difficulty because the permeability of the metals under consideration is practically unity so long as they are in the normal state. This theory however asserts that the appearance of superconductivity cannot by itself alter the field. The lines of force would still go through the specimen undeviated. On the contrary, Meissner and Ochsenfeld²² showed in 1933 that the final

¹⁹ If I is measured in amperes and H in oersteds $H = 0.2 I/R$.

²⁰ F. B. Silsbee, *J. Washington Acad. Sci.*, 6, 597 (1916); Pap. Bureau of Standards 14, 307 (1917).

²¹ L. W. Shubnikov and N. E. Alexejevski, *Nature*, 188, 804 (1936).

²² W. Meissner and R. Ochsenfeld, *Naturwissenschaften*, 21, 787 (1933).
W. Meissner, *Physik. Z.*, 85, 931 (1934).

state is in fact identical in the two cases — it does not depend on the previous history. In a singly connected superconductor everything is uniquely determined by its temperature and the apparatus producing the external field: in an n -ply connected body there is a possibility of $n - 1$ persistent currents and their magnetic fields whose strengths are optional within certain limits. But in any case the interior of a sufficiently thick superconductor is field free. The field-free state is the only state in such a superconductor.

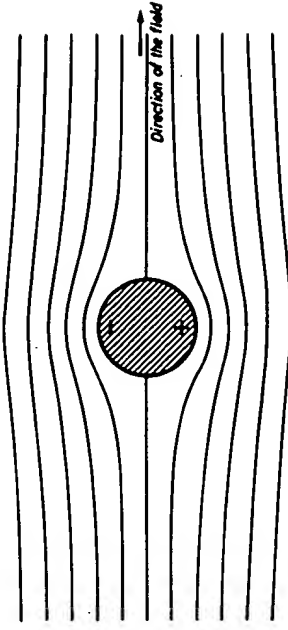


Fig. 1—5. The transverse field near a superconducting circular cylinder. The lines of force are plotted from the equation, in polar coordinates:

$$(r - R^2/r) \sin \theta = C \quad \text{for } C = 0, \pm 1/2 R, \pm R, \pm 3R/2, \pm 2R, \pm 5R/2.$$

+ or — means the supercurrent flows toward or away from the reader respectively.

This fact permits us to interpret the super- and normal conductors as two phases of the same substance, whereas according to the older theory the state inside the superconductor was not determined intrinsically. Under this condition we can now apply thermodynamics to the equilibrium between the normal and the superconducting state (see Chap. 17). The London extension of the Maxwell theory is also based essentially on the expulsion of the field, called the Meissner effect.

(g) The older conception permitted us to calculate the field deformation near a thick superconductor accurately enough when the cooling precedes the application of the field. It showed that the distortion of the lines of force at certain points of the surface increases the field strength (see Fig. 1-5); for a superconducting sphere in a homogeneous field by a maximum factor $3/2$, for a circular cylinder in a transverse field by a factor 2, and for an elliptical cylinder with cross-sectional axes a and b by the factor $(1 + b/a)$ when the field is parallel to the a axis.

It was thus possible in 1932 — even before the Meissner discovery — for the author²³ to explain the fact that a transverse external field $1/2 H_c$ was sufficient to quench the superconductivity in a wire. It was also predicted that an elliptical cylinder would show a greater decrease of the apparent

²³ M. v. Laue, *Physik. Z.*, 88, 793 (1932).

critical value than a circular cylinder if the field were perpendicular to the greater axis; also for a sphere the apparent critical value would amount to $(2/3)H_c$ (see Chap. 10 (c) and (d), and Chap. 11). All these predictions were confirmed by an extensive series of measurements by de Haas and co-workers^{24 25 26}. In this work it was also found that the most certain indication of the breakdown of superconductivity was not the reappearance of an ohmic resistance, but the appearance of a magnetic field in the interior of the specimen as detected by means of small bismuth wires placed in cavities in the specimen. The whole specimen does not immediately become normally conducting with the disappearance of superconductivity; instead the "intermediate state" almost always appears, a mechanical mixture of normal and superconducting parts (Chap. 19). As long as the latter form a connected path they take over the conduction of the current exclusively.

(h) Finally our book will discuss thermal measurements, e. g., the heat required in the transition to normal from superconducting states, whenever this takes place in a magnetic field; or the specific heats of the normal and superconductors. But we shall postpone any more detailed discussion of this until Chap. 17 where the thermodynamics will reveal relations between these caloric phenomena and the critical magnetic field.

CHAPTER 2

Current Distribution Between Superconductors in Parallel

(a) If between two points of a normally conducting system there are n branches with resistances r_1, r_2, \dots, r_n , then the ratios of the direct currents are

$$I_1 : I_2 : \dots : I_n = \frac{1}{r_1} : \frac{1}{r_2} : \dots : \frac{1}{r_n}$$

This rule of Kirchhoff's remains valid when one branch becomes superconducting, e. g., $r_n = 0$. This states that $I_1 = I_2 = \dots = I_{n-1} = 0$; i. e., the superconductor short-circuits all the other branches. If we apply an emf to such a system consisting of one and the same metal above the transition temperature, then the rule still holds even if we cool the metal until superconductivity appears. The appearance of superconductivity—does not change the individual currents if the total current $\sum_{k=1}^n I_k$ is kept constant. As a matter of fact any (possible) cause for such a change disappears as the mutual inductions between all the currents I_k vanish.

²⁴W. J. de Haas and J. M. Casimir-Jonker, *Physica*, 1, 291 (1934).

²⁵W. J. de Haas and O. A. Guineau, *Physica*, 1, 291 (1934).

²⁶W. J. de Haas, A. D. Engelkes, and O. A. Guineau, *Physica*, 4, 595 (1937).

If initially all values of $r_k = 0$, the Kirchhoff rule cannot be applied at all. The calculation of the current distribution must be based upon the fact that the current is initiated by means of a voltage V , formed between the junctions, which changes with time and dies out as soon as the currents become stationary, the whole process being described in terms of the laws of induction. In using these laws we have to assume that the inductive coupling between the n branches is much stronger than their coupling with the leads to the junctions. This condition is fulfilled by inserting coils with considerable mutual inductance in the branches and by having the leads in the form of straight wires which do not come too close to the coils. The magnetic field of the system is then mainly confined to the vicinity of the coils.

Under these conditions the magnetic field strength H is a linear function of the currents I_k at every point; the energy density $\frac{1}{2}H^2$ and also the total magnetic energy

$$\frac{1}{2} \int H^2 dx dy dz = \frac{1}{2} \sum_{k,l} p_{kl} I_k I_l$$

is therefore a quadratic form in I_k . This form is necessarily positive and definite, i. e., all p_{kl} , the determinant of the p_{kl} , as well as all subdeterminants symmetrical with respect to the diagonal, are positive. For $n = 2$,

$$p_{11} > 0, \quad p_{22} > 0, \quad p_{11}p_{22} - p_{12}^2 > 0 \quad (2-1)$$

The p_{kl} are the coefficients of self induction, the "mixed" terms p_{kl} are the coefficients of mutual induction. $p_{kl} = p_{lk}$ identically.

It is possible to derive Maxwell's equations from the principle of least action by considering the electric energy as the potential energy and the magnetic energy as the kinetic energy. If electric currents are flowing, the work $V \cdot \delta e$ performed by the emf's has to be taken into consideration, where δe is the amount of electricity transported in a given direction by the current I . Here we have to do with quasi-stationary processes for which the electric energy vanishes compared with the magnetic energy. Under the assumption that the magnetic energy is the only energy depending on the currents, this principle now reads:

$$\delta \int \left(\frac{1}{2} \sum_{k,l} p_{kl} I_k I_l - V \sum_k e_k \right) dt = 0 \quad (2-2)$$

As $-I_k = de_k/dt$ is the velocity corresponding to the coordinate e_k , the corresponding Euler equations are

$$\frac{d}{dt} \left(\sum_l p_{kl} I_l \right) - V = 0 \quad (k = 1, 2, \dots, n) \quad (2-3)$$

and we recognize these as the usual induction equations. They are immediately integrable with respect to time t , and if all I_k are zero at $t = 0$ we obtain

$$\sum_i \dot{p}_{ki} I_i = \int V dt \quad (2-4)$$

This holds for all times, including the final state in which all I_k have become stationary and $V = 0$ by eq. (2-3). Unfortunately the quantity $\int V dt$ is not determined by the experiment, but only the current $I = \sum_k I_k$ in the steady state, namely by a galvanometer in the leads. However, together with the equation $I = \sum_k I_k$, eq. 2-4 forms $n + 1$ linear relations between the $n + 1$ unknowns I_1, I_2, \dots, I_n and $\int V dt$. For the special case $n = 2$, eq. 2-4 gives

$$\dot{p}_{11} I_1 + \dot{p}_{12} I_2 = \dot{p}_{21} I_1 + \dot{p}_{22} I_2 = \int V dt \quad (2-5)$$

Therefore because $I_1 + I_2 = I$ we have

$$I_1 = \frac{\dot{p}_{22} - \dot{p}_{12}}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I \quad I_2 = \frac{\dot{p}_{11} - \dot{p}_{12}}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I \quad (2-6)$$

We regard I as positive; a positive I_k means that this current flows in the same direction as I ; a negative I_k means that it has the opposite direction.

According to eq. 2-1 and because the geometric mean of two positive quantities lies below the arithmetic mean:

$$|\dot{p}_{12}| < \sqrt{\dot{p}_{11}\dot{p}_{22}} < \frac{1}{2}(\dot{p}_{11} + \dot{p}_{22})$$

The denominator in eq. 2-6 is therefore always positive. However, it may very well be that $\dot{p}_{12} > \dot{p}_{22}$; but then because of eq. 2-1 $\dot{p}_{11} > \dot{p}_{12}$. In this case $I_2 > I$, $I_1 < 0$. The current in the first branch flows opposite to the input current, an impossible occurrence in normal conduction.¹ After they were derived theoretically by the author,² eq. 2-6 including the last inference, was confirmed quantitatively by Justi and Zickner.³

If a current I^0 was already flowing at time $t = 0$, with branch currents I_1^0 and I_2^0 , then these currents are superimposed on the system under consideration: in the first branch the current $I_1 + I_1^0$ will now flow, in the second $I_2 + I_2^0$. If in particular $I^0 = -I$, then, as can easily be computed, $I_1 + I_1^0 = -(I_2 + I_2^0)$, and the leads carry no current. Therefore if we have introduced a current before cooling down to the superconducting state, and after the cooling we cut off the supply leads, then a persistent current remains in the ring consisting of the two branches. We recognize here a second method of producing persistent currents. This

¹ Under certain circumstances it may happen that the absolute value of I_1 can be greater than I .

² See Chap. 1, footnote 23.

³ E. Justi and G. Zickner, *Phys. Z.*, 42, 258 (1941).

has also been proved experimentally by Justi and Zickner. If we now feed in still another current I' , then this is independent of the persistent current, and its branch currents I_1' and I_2' calculated from eq. 2-6 are superimposed on the persistent current.

(b) Equation 2-4 allows yet another interpretation. If we ask which distribution of the current I minimizes the magnetic energy $1/2 \sum_k \dot{p}_{ki} I_i$, using the Lagrange undetermined multiplier κ we find the conditions

$$\left(\frac{\partial}{\partial I_i}\right) \left(\frac{1}{2} \sum_{kl} \dot{p}_{kl} I_k I_l - \kappa \sum_k I_k \right) = 0$$

$$\sum_k \dot{p}_{ki} I_k = \kappa \quad (i = 1, 2, \dots, n)$$

However, from this and from

$$\sum_i I_i = I$$

we get the same relations between the I_i and I as from eq. 2-4. The current distribution in the branched superconducting circuit adjusts itself so as to minimize the magnetic energy. This minimum is, according to eq. 2-6,

$$\frac{1}{2} \frac{\dot{p}_{11}\dot{p}_{22} - \dot{p}_{12}^2}{\dot{p}_{11} + \dot{p}_{22} - 2\dot{p}_{12}} I^2$$

This is important for the understanding of Sizoo's experiments.⁴ In fact, in his experiment, $\dot{p}_{11}\dot{p}_{22} - \dot{p}_{12}^2$ is very nearly zero. On supplying a current, no magnetic field at all is produced — to this approximation; the field strength remains zero at every point in space. If before feeding in I there are already two currents I_1^0 and I_2^0 flowing in the branches which produce a magnetic field because they are not in the ratio $I_1 : I_2$, then this addition of I does not change anything in the magnetic field; a new field is merely superimposed on the old one, which in our case is zero. This conclusion also remains valid if we choose $I = -(I_1^0 + I_2^0)$, i. e., if we simply cut off the leads. All this had been found experimentally by Sizoo in 1926 and it was his work that instigated the discussion presented here.

According to eq. 2-5

$$(\dot{p}_{11} - \dot{p}_{21}) I_1 - (\dot{p}_{22} - \dot{p}_{12}) I_2 = 0$$

In the approximation used here, which allows us to ascribe its own induction coefficient to each of the two unclosed branches (strictly speaking only for closed circuits), the left-hand side of this equation is the flux of induction through the superconducting ring formed by the two branches. The fact that the flux of induction retains its initial value, i. e., zero, even if currents are switched on, corresponds to a theorem which will be discussed in general in Chap. 12.

⁴ G. J. Sizoo, Thesis, Leiden, 1926.

(c) The experiments under discussion not only confirm the complete disappearance of the resistances r_k but also show that there is no noticeable amount of any other energy depending on the current to be added to the magnetic energy. Such an energy would have to be added to the magnetic energy in the principle of least action, equation 2-2, and would disturb the linearity of the relations between the I_k and I , if it were a quadratic function of the I_k . Otherwise it would at least cause the induction coefficients applicable to these experiments to deviate from the p_M values as measured with ohmic currents. Neither possibility occurs in practice. We shall find in Chaps. 5 and 12 that a specific superconduction energy actually does appear, but that in the experiments under discussion and in many other similar experiments, it is far too small an amount to show up against the magnetic energy.

As we indicated in Chap. 1 (c), superconductors have an ohmic resistance for varying currents, in spite of the fact that their d. c. resistance is zero. In the measurements mentioned in this paragraph however the variations were much too slow for this effect to be appreciable.

CHAPTER 3

Fundamental Equations of the Maxwell-London Theory^{1,2}

(a) In most experimental work we observe effects on the field surrounding the superconductor caused by the phenomena occurring inside the superconductor. To be of any value, therefore, the theory must retain Maxwell's equations for empty space. We shall simplify the Maxwell equations by limiting the discussion to isotropic substances or cubic crystals. This restriction can easily be lifted if necessary, but so far no such necessity has arisen. We therefore introduce the three vectors \mathbf{E} , \mathbf{D} , and \mathbf{i} , the first of which is the field intensity, the second the displacement, and the third the current density. There exist between them the relations

$$\mathbf{D} = \epsilon \mathbf{E} \quad \mathbf{i} = \sigma \mathbf{E} \quad (3-1)$$

The dielectric constant ϵ and the conductivity σ are positive constants of the material depending only on temperature. For the magnetic field we need three more vectors \mathbf{H} , \mathbf{B} , and \mathbf{M} , i. e., the field intensity, the magnetic induction, and the induction due to permanent magnetization present only in permanent magnets that may be in the field. For these we have the relation

¹F. London, Une conception nouvelle de la supraconductivité, Paris, 1937.

²M. v. Laue, (a) *Ann. Physik*, 48, 65 (1942); (b) 48, 223 (1943); (c) 2, 183 (1948); (d) 8, 31 (1948); (e) 8, 40 (1948); (f) *Z. Physik*, 155, 517 (1949).

$$\mathbf{B} = \mu \mathbf{H} + \mathbf{M} \quad (3-2)$$

Here μ is a constant depending only on temperature, taken to be unity for ferromagnetics where \mathbf{M} is not zero. Hysteresis effects are not included in eq. 3-2, it is true, except implicitly in the behavior of \mathbf{M} . In Lorentz units, which we shall use throughout unless specifically stated otherwise, the Maxwell equations themselves now have the form

$$\begin{array}{ll} \text{I} & \text{curl } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \\ \text{II} & \text{curl } \mathbf{H} = \frac{1}{c} \left(\frac{\partial \mathbf{D}}{\partial t} + \mathbf{i} \right) \\ \text{III} & \text{div } \mathbf{B} = 0 \\ \text{IV} & \text{div } \mathbf{D} = \rho \end{array}$$

ρ is the space charge density.

(b) For the superconductor we put $\epsilon = 1$ from the outset, as Maxwell's theory does for all metallic conductors. An important feature of London's generalization is that the permeability $\mu = 1$. Moreover, $\mathbf{M} = 0$, because no ferromagnetic material shows superconductivity. So \mathbf{D} coincides with \mathbf{E} and \mathbf{B} with \mathbf{H} . Equations I — IV are simplified to

$$\begin{array}{ll} \text{I}_s & \text{curl } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} \\ \text{II}_s & \text{curl } \mathbf{H} = \frac{1}{c} \left(\frac{\partial \mathbf{E}}{\partial t} + \mathbf{i} \right) \\ \text{III}_s & \text{div } \mathbf{H} = 0 \\ \text{IV}_s & \text{div } \mathbf{E} = \rho \end{array}$$

Now — and this introduces something essentially new — the current \mathbf{i} and the density ρ are each split into two parts by this theory, namely the ohmic current \mathbf{i}^0 together with the appropriate density ρ^0 , and the supercurrent \mathbf{i}^s with the corresponding density ρ^s .

$$\mathbf{i} = \mathbf{i}^0 + \mathbf{i}^s \quad \rho = \rho^0 + \rho^s$$

Between each sort of current and the corresponding density we assume a continuity equation:

$$\text{VI} \quad \text{div } \mathbf{i}^0 + \frac{\partial \rho^0}{\partial t} = 0, \quad \text{div } \mathbf{i}^s + \frac{\partial \rho^s}{\partial t} = 0$$

Equation VI gives a definite meaning to the coupling of ρ^0 with \mathbf{i}^0 and of ρ^s with \mathbf{i}^s . Only the continuity equation for the total current \mathbf{i} and the total density ρ follows in the known way from II_s and IV_s. The subdivision carried out here therefore represents an essentially new assumption. Incidentally, ρ^0 shall include not only the contribution from the mobile carriers of the ohmic current \mathbf{i}^0 , but also that from the fixed atoms which is constant in time, and for a homogeneous superconductor uniform in space. This is completely consistent with eq. VI. ρ^s shall be due only to the carriers of the supercurrent. We are forced to this assertion because in eq. 13-10 ρ^s appears as a factor in a product which can be related only to the supercurrent.

For the ohmic current, Ohm's law, i. e., a linear relationship between \mathbf{i}^0 and \mathbf{E} , shall still be valid in superconductors. For a crystal it always has the form

$$\text{VII} \quad \mathbf{i}^0 = \sum_{\beta} \sigma_{\alpha\beta} \mathbf{E}_{\beta}$$

and for mathematical reasons $\sigma_{\alpha\beta}$ is a tensor of the second rank which we call the conductivity tensor. For cubic crystals it simplifies to a scalar conductivity σ , and eq. VII is replaced by the equation

$$\text{VIIa} \quad \mathbf{i}^0 = \sigma \mathbf{E}$$

The $\sigma_{\alpha\beta}$ are of the dimensions t^{-1} . The order of magnitude of σ and likewise the principal values $\sigma_{\alpha\alpha}$ of the tensor for normally conducting pure metals at the low temperatures under discussion is of the order 10^{10} sec^{-1} . According to experiments to be described in Chap. 16, we may also ascribe the same order of magnitude to the superconductor in spite of the fact that actual measurements are not available.

Finally, London's fundamental equations for the supercurrent appear as essentially new equations in the theory. We formulate them for an arbitrary crystal by associating with the vector \mathbf{i} a vector \mathbf{G} for the super-momentum per unit charge and by postulating a linear relation between them in terms of the tensor³ $\lambda_{\alpha\beta}$ the sums being over $\alpha, \beta = 1, 2, 3$:

$$\text{VIII} \quad \mathbf{G}_{\alpha} = \sum_{\beta} \lambda_{\alpha\beta} \mathbf{i}^{\beta}$$

which simplifies for cubic crystals to read

$$\text{VIIIa} \quad \mathbf{G} = \lambda \mathbf{i}$$

And for \mathbf{G} we introduce the following two differential equations due to London⁴

$$\text{IX} \quad \frac{\partial \mathbf{G}}{\partial t} = \mathbf{E} \quad \text{X} \quad c \text{ curl } \mathbf{G} = -\mathbf{H}$$

According to Chap. 1 (c), London's constant λ is a function of temperature that increases beyond all limit as we approach the transition temperature

³This tensor was introduced by M. von Laue (see footnote 2d).

⁴These equations can be combined relativistically in the form

$$c \left(\frac{\partial P_m}{\partial x_n} - \frac{\partial P_n}{\partial x_m} \right) = M_{nm} \quad m, n = 1, 2, 3, 4$$

if one puts $M_{14} = -iE_1$, etc., $M_{23} = H_1$ etc., and $x_4 = ict$; the four vector \mathbf{P} is reduced to the supermomentum by identifying $P_{\alpha} = G_{\alpha}$, $\alpha = 1, 2, 3$, and $P_4 = 0$ for the system at rest.

Here we have written x_1, x_2 , and x_3 for x, y, z , but this can scarcely lead to any misunderstanding.

from below. The tensor $\lambda_{\alpha\beta}$ must have the same property. The dimensions of its components are $[\text{time}]^2$.

The most general tensor of second rank is asymmetrical, but from Table 1-1 all the crystal classes in which superconductivity has been observed have such high crystallographic symmetry that all tensor constants must be symmetrical, i. e., interchanging their suffixes does not change their value.⁵ We therefore put

$$\begin{aligned} \sigma_{\alpha\beta} &= \sigma_{\beta\alpha} \\ \lambda_{\alpha\beta} &= \lambda_{\beta\alpha} \end{aligned} \quad (3-3)$$

In Chap. 13 (b) this will turn out to be a necessary condition for the possibility of superconductivity. It can also be understood in this way why deformations which distort the natural symmetry of the crystals easily destroy the superconductivity — as has often been observed.

We shall find in Chap. 5 that

$$\frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) = \frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}^{\alpha} \mathbf{i}^{\beta} \quad (3-4)$$

is the density of the free energy that is connected with the supercurrent. By requiring that it be positive, not only in the cubic system where it equals $\frac{1}{2} \lambda (\mathbf{i}^0)^2$, but also under all circumstances, we conclude that the components $\lambda_{\alpha\alpha}$ with two identical suffixes, the determinant of all the $\lambda_{\alpha\beta}$, and the three symmetrical subdeterminants

$$\begin{vmatrix} \lambda_{\alpha\alpha} & \lambda_{\alpha\beta} \\ \lambda_{\beta\alpha} & \lambda_{\beta\beta} \end{vmatrix}$$

are all positive. These are the necessary and sufficient conditions that the quadratic form $\sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}^{\alpha} \mathbf{i}^{\beta}$ shall be positive and definite. But as $\sum_{\alpha\beta} \sigma_{\alpha\beta} \mathbf{E}_{\alpha} \mathbf{E}_{\beta}$ is also positive and definite (it is the expression for the Joule heat, see Chap. 5), the conductivity tensor obeys the same conditions. The quadratic surfaces corresponding to these tensors:

$$\sum_{\alpha\beta} \lambda_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant} \quad \text{and} \quad \sum_{\alpha\beta} \sigma_{\alpha\beta} x_{\alpha} x_{\beta} = \text{constant}$$

are therefore ellipsoids. If their axes are chosen as coordinates, then all the tensor components with unlike suffixes vanish, and those with two like suffixes give the principal values $\lambda_1, \lambda_2, \lambda_3$ of the tensor.

In the crystal classes in which superconductivity has been detected to date (Table 1-1) the axes of these ellipsoids are completely fixed and

⁵This is also true for all superconducting compounds and alloys. Compare Max von Laue, footnote 2c; in this reference, a table appears giving all crystal classes together with the properties of all second-rank tensors that can belong to them, like the tensors $\lambda_{\alpha\beta}$ and $\sigma_{\alpha\beta}$, that can form a linear relation between two polar vectors. In these particular cases the polar vectors are \mathbf{i} and \mathbf{G} , \mathbf{i}^0 , and \mathbf{E} .

coincide with the principal crystallographic axes. In the rhombic system, i. e., for gallium and uranium, they are mutually perpendicular but not of equal length. In the tetragonal and hexagonal systems the surfaces are ellipsoids of revolution whose unequal axes coincide with the principal crystallographic axes. Therefore two of the principal values of the tensor are equal. We need scarcely mention the cubic system for which the ellipsoid degenerates into a sphere.

As the determinant of $\lambda_{\alpha\beta}$ differs from zero the three equations VIII can be solved for the components $\dot{\mathbf{r}}_\alpha$. Thus not only does it follow from $\dot{\mathbf{r}} = 0$ that $\dot{\mathbf{G}} = 0$, but also conversely from $\dot{\mathbf{G}} = 0$ that $\dot{\mathbf{r}} = 0$.

It is a significant feature of this theory that the ohmic current and the supercurrent are essentially independent of each other and are only coupled in a secondary way through the magnetic field with which they are both related.

The fundamental equations of this chapter are not all independent. Equation III, is given by forming the divergence of $\dot{\mathbf{X}}$; eq. I, by forming the curl of eq. IX and using eq. X. Nevertheless by retaining eqs. I, and III, we show more clearly that the London theory does not do away with the Maxwell theory, but only supplements it. There is no contradiction in the system of equations.

(c) In addition to the differential equations, the theory still needs to be completed by boundary conditions at all surfaces where the constants of the theory undergo sudden changes, as at the surface of the specimen. Such boundary conditions do not represent new additions; they are limiting forms of the differential equations themselves. For instance \mathbf{B} , \mathbf{D} , and \mathbf{i} have finite time derivatives everywhere, and hence eqs. I and II lead through Stokes' theorem regarded as applying to a "surface curl" to the result that the tangential components of both fields are continuous across any surface. Also, according to eq. III we may say that the "surface divergence" of \mathbf{B} is zero; therefore if we indicate two opposite normals of the surface of discontinuity by n_1 and n_2 we obtain

$$\mathbf{B}_{n_1} + \mathbf{B}_{n_2} = 0 \quad (3-5)$$

Similarly, according to eq. IV, when a surface charge density exists we have

$$\mathbf{D}_{n_1} + \mathbf{D}_{n_2} = \rho \quad (3-6)$$

These two equations hold for the superconductor if we replace \mathbf{B} by \mathbf{H} and \mathbf{D} by \mathbf{E} . The following new boundary conditions then have to be added: according to the continuity equations in eq. VI the surface divergences of the current densities $\dot{\mathbf{i}}^0$ and $\dot{\mathbf{i}}$ are related to the surface charge densities ρ^0 and ρ by the equations:

$$\dot{\mathbf{i}}^0_{n_1} + \dot{\mathbf{i}}^0_{n_2} = \frac{\partial \rho^0}{\partial t} \quad \dot{\mathbf{i}}_{n_1} + \dot{\mathbf{i}}_{n_2} = \frac{\partial \rho}{\partial t} \quad (3-7)$$

Finally because \mathbf{H} is finite everywhere, eq. X requires that the tangential components of $\dot{\mathbf{G}}$ be everywhere continuous across every surface:

$$\mathbf{G}_\alpha = \dot{\mathbf{G}}_\alpha, \quad (3-8)$$

This means that at the boundary between two cubic crystal superconductors

$$\lambda_1 \dot{\mathbf{r}}_{\alpha_1} = \lambda_2 \dot{\mathbf{r}}_{\alpha_2}, \quad (3-9)$$

The superconductor with the smaller λ carries the higher tangential current; it behaves as if it were the better superconductor. Increasing temperature increases the constant, as already stated, thus impairing the superconductor.

(d) Although, as already mentioned, we shall generally use Lorentz units, we have also enumerated the changes involved in the transition to electrostatic units. In these units the fundamental eqs. II and IV become

$$\text{curl } \mathbf{H} = \frac{1}{c} \left(\frac{\partial \mathbf{D}}{\partial t} + 4\pi \mathbf{i} \right) \quad \text{and} \quad \text{div } \mathbf{D} = 4\pi \rho$$

Equations I, III, and VII remain unchanged. In general, the transformation is effected by the equations:

$$\begin{aligned} \rho_L &= \sqrt{4\pi} \rho_{EI}, & \mathbf{i}_L &= \sqrt{4\pi} \mathbf{i}_{EI}, & \mathbf{E}_L &= \frac{\mathbf{E}_{EI}}{\sqrt{4\pi}}, \\ \mathbf{H}_L &= \frac{\mathbf{H}_{EI}}{\sqrt{4\pi}}, & \mathbf{B}_L &= \frac{\mathbf{B}_{EI}}{\sqrt{4\pi}}, & (\sigma_{\alpha\beta})_L &= 4\pi (\sigma_{\alpha\beta})_{EI} \end{aligned} \quad (3-10)$$

The question arises: shall the tensor components $\lambda_{\alpha\beta}$ have the same values in both systems so that $\mathbf{G}_L = \sqrt{4\pi} \mathbf{G}_{EI}$ and the eqs. IX and X have to be replaced by

$$4\pi \frac{\partial \mathbf{G}_{EI}}{\partial t} = \mathbf{E} \quad \text{and} \quad 4\pi c \text{ curl } \mathbf{G}_{EI} = -\mathbf{H}?$$

We decide instead in favor of taking over eqs. IX and X unchanged in the electrostatic system and derive the transformations:

$$\mathbf{G}_L = \frac{\mathbf{G}_{EI}}{\sqrt{4\pi}}, \quad (\lambda_{\alpha\beta})_L = \frac{(\lambda_{\alpha\beta})_{EI}}{4\pi} \quad (3-11)$$

We shall find out the advantages of this convention in Chaps. 15 and 16. There the pure number $v\sigma\lambda$, where v is a frequency, has the same value in both systems of units, and plays an important part in the theory of oscillations similar to the part played by the scalar product $(\dot{\mathbf{r}} \cdot \mathbf{G})$ in what follows.

(e) Even though we intend to present London's theory in a phenomenological manner, we wish nevertheless to point out the atomic theory basis from which it developed historically. Fritz and Heinz London⁶ attempted in 1935 to make the fundamental eqs. IX and X, which they wrote in the form

$$\text{IXa} \quad \frac{\partial \lambda \dot{\mathbf{r}}}{\partial t} = \mathbf{E} \quad \text{Xa} \quad c \text{ curl } (\lambda \dot{\mathbf{r}}) = -\mathbf{H}$$

⁶F. and H. London, *Physica*, 2, 241 (1935).

seem plausible from quantum theoretical considerations. In this way they found a relation between the constant λ and the charge e , the mass m of the electron, and the number N of the superconducting electrons per unit volume, namely,

$$\lambda = \frac{m}{e^2 N} \quad (3-12)$$

However, eq. IXa had already been derived in 1933 by Becker, Heller, and Sauter⁷ on a purely mechanical basis. They took the electric field as the only force acting on the electron, so that

$$m \frac{dv}{dt} = eE$$

where v is the velocity of the electron. Furthermore, as the current density is $i^* = eNv$ one arrives at eqs. IXa and 3-12 if one neglects the difference between the partial time derivative $\partial/\partial t$ (at constant coordinates) and d/dt (referring to a moving particle): this is permissible for sufficiently small velocities. Equation Xa can be derived from eq. IXa by means of Maxwell's equation I under the physically self-evident assumption that no field existed prior to a certain time 0. Thus if one takes the curl of eq. IXa and integrates from $t = 0$ to t , one gets:

$$\text{curl}(\lambda i^*) = \int_0^t \text{curl} E dt = -\frac{1}{c} H$$

To this extent this entire theory was contained in the "acceleration theory" of Becker and co-workers.

We shall not go further into this atomic picture here although in Chap. 13 we shall make use of the picture to explain the Maxwell-London stresses, assuming that neither the lattice formed by the ions nor the ohmic conduction electrons exert any force on the mechanism of the supercurrent.

To make a rough estimate of λ from 3-12 we take aluminum as an example. The lattice cell contains four atoms and has an edge of 4×10^{-8} cm. In one cubic centimeter therefore there are 1.6×10^{22} cells and 6.4×10^{22} atoms. If we assume the number N of superconducting electrons to be the same, with $m = 9 \times 10^{-28}$ gm and $e_L = \sqrt{4\pi e_{EI}} = \sqrt{4\pi \times 4.8 \times 10^{-10}} = 1.7 \times 10^{-9}$ Lorentz unit, it follows that

$$\lambda_L = 2 \times 10^{-32} \text{ sec}^2 \quad (3-13)$$

or according to 3-11.

$$\lambda_{EI} = 2.5 \times 10^{-31} \text{ sec}^2$$

But probably the number N is much smaller, and λ accordingly greater.

⁷R. Becker, G. Heller, and F. Sauter, *Z. Physik*, **85**, 772 (1933).

CHAPTER 4

Space Charges in Superconductors

Space charges may be formed in a superconductor by irradiating it with fast cathode rays which are sooner or later trapped inside the superconductor. The theory must lead to plausible conclusions about the future of such charges, and this requirement has played a role in its development. We assume the crystal to be cubic, λ and σ constants in space and time. From eqs. VI, IXa, and IVa respectively there follow the equations

$$\frac{\partial^2 \rho^s}{\partial t^2} = -\text{div} \frac{\partial i^s}{\partial t} = -\frac{1}{\lambda} \text{div} E = -\frac{\rho}{\lambda} = -\frac{(\rho^0 + \rho^s)}{\lambda}$$

while from eqs. IV, VIIa, and VI correspondingly

$$\rho = \text{div} E = \frac{1}{\sigma} \text{div} i^0 = -\frac{1}{\sigma} \frac{\partial \rho^0}{\partial t}$$

Therefore the differential equations

$$\frac{\partial^2 \rho^s}{\partial t^2} + \frac{(\rho^0 + \rho^s)}{\lambda} = 0 \quad \frac{\partial \rho^0}{\partial t} + \sigma(\rho^0 + \rho^s) = 0 \quad (4-1)$$

hold for the two unknowns ρ^s and ρ^0 . They are solved under the assumption that

$$\rho^0 = P^0 e^{-at} \quad \rho^s = P^s e^{-at} \quad (4-2)$$

which transform the differential equations into the algebraic relations

$$(\alpha^2 + \lambda^{-1}) P^s + \lambda^{-1} P^0 = 0 \quad (4-3)$$

$$\sigma P^s + (\sigma - a) P^0 = 0$$

Putting the determinant of the coefficients equal to zero yields for a the equation

$$\alpha^3 - \sigma\alpha^2 + \lambda^{-1}\alpha = 0 \quad (4-4)$$

To each root of this equation there corresponds a certain ratio P^s/P^0 . Carrying through the calculation gives

$$\alpha_1 = \frac{1}{2}(\sigma + \sqrt{\sigma^2 - 4\lambda^{-1}}), \quad \left(\frac{P^s}{P^0}\right)_1 = -\frac{1}{2}\left(1 - \sqrt{1 - \frac{4}{\sigma^2\lambda}}\right)$$

$$\alpha_2 = \frac{1}{2}(\sigma - \sqrt{\sigma^2 - 4\lambda^{-1}}), \quad \left(\frac{P^s}{P^0}\right)_2 = -\frac{1}{2}\left(1 + \sqrt{1 - \frac{4}{\sigma^2\lambda}}\right) \quad (4-5)$$

$$\alpha_3 = 0, \quad \left(\frac{P^s}{P^0}\right)_3 = -1$$

The general solution of eq. 4-1 therefore reads

$$\begin{aligned} \rho^0 &= A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t} + A_3 \\ \rho^s &= -\frac{1}{2}\left(1 - \sqrt{1 - \frac{4}{\sigma^2\lambda}}\right) A_1 e^{-\alpha_1 t} - \frac{1}{2}\left(1 + \sqrt{1 - \frac{4}{\sigma^2\lambda}}\right) A_2 e^{-\alpha_2 t} - A_3 \end{aligned}$$

A_1, A_2, A_3 are constants of integration, i. e., invariable with time, but otherwise arbitrary functions of position. α_1 and α_2 can be complex, but both roots always have real parts. When α_1 and α_2 are complex, there are superposed vibrations of ρ^0 and ρ^s which decay with time until $\rho = \rho^0 + \rho^s$ becomes zero. The equations do not require that the individual densities ρ^0 and ρ^s each vanish. This is related to the fact that the two mechanisms of conduction are independent, being coupled only by the field which has already disappeared in the final state when the total density $\rho = 0$.

On the whole the phenomenological theory does not say anything about the individual densities in the final state, except that where a current i is flowing, ρ^s cannot be zero. Otherwise the momentum $\rho^s \lambda i$ of the supercurrent, which we shall meet with in eq. 13-10, should equally well be zero. Because the field equations are linear, the decay of ρ takes place independently of, and is superimposed upon, all other processes that occur in the superconductor. When we investigate these other processes, therefore, we neglect the space charge completely and always put $\text{div } \mathbf{E} = 0$ in place of IV.

In order to do this it is necessary that σ and λ do not change in time or space. If these constants were to vary because of temperature inequalities for example, or varying composition of an alloy, then the space charges would change according to other laws. Nevertheless in a stationary state the superconductor is charge free under all circumstances. From eq. VIII it follows, namely, that if $\partial/\partial t = 0$, then $\mathbf{E} = 0$, and therefore according to eq. IV, $\rho = 0$. The above calculation cannot be applied to a noncubic crystal where σ is a symmetrical tensor. However, in the next chapter we will show how we can also draw conclusions about the decay in this case. In a normal conductor with a cubic lattice the charge decays according to $e^{-\sigma t}$ as can be seen by forming the divergence of eq. III. This result is well known, but having regard to the magnitude of σ it is doubtful whether the Maxwell theory will still be valid for such a rapid decay. It is also doubtful in our theory of superconductivity. However, it is significant that the theory does lead to plausible results, and its conclusions about the decay should be at least qualitatively correct.

CHAPTER 5

The Conservation of Energy

(a) We obtain the energy principle for the space outside the superconductor in the known manner by forming the scalar product of eq. I with $(-\mathbf{H})$ and of II with \mathbf{E} , adding the results and applying the rule

$$(\mathbf{P} \cdot \text{curl } \mathbf{Q}) - (\mathbf{Q} \cdot \text{curl } \mathbf{P}) = \text{div } [\mathbf{Q} \times \mathbf{P}] \quad (5-1)$$

The result is immediately

$$-c \text{div } [\mathbf{E} \times \mathbf{H}] = \left(\mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} \right) + \left(\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} \right) + (\mathbf{E} \cdot \mathbf{i}) \quad (5-2)$$

According to eqs. 3-1 and 3-2 and because $\partial \mathbf{M}/\partial t = 0$, this takes the form

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \epsilon \mathbf{E}^2 + \frac{1}{2} \mu \mathbf{H}^2 \right) + \sigma \mathbf{E}^2 + c \text{div } [\mathbf{E} \times \mathbf{H}] = 0 \quad (5-3)$$

Within the differential sign are the density of electrical energy $\frac{1}{2} \epsilon \mathbf{E}^2$ and of magnetic energy $\frac{1}{2} \mu \mathbf{H}^2$; $\sigma \mathbf{E}^2$ gives the Joule heat per unit time, and $c [\mathbf{E} \times \mathbf{H}]$ is the flux density of electromagnetic energy, the so-called Poynting vector.

Proceeding in the same manner with eqs. I, and II, we find for the interior of the superconductor, instead of eq. 5-2

$$-c \text{div } [\mathbf{E} \times \mathbf{H}] = \left(\mathbf{E} \cdot \frac{\partial \mathbf{E}}{\partial t} \right) + \left(\mathbf{H} \cdot \frac{\partial \mathbf{H}}{\partial t} \right) + (\mathbf{E} \cdot \mathbf{i}^0) + (\mathbf{E} \cdot \mathbf{i}^s) \quad (5-4)$$

or, also according to eqs. VII, VIII, and IX

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \mathbf{E}^2 + \frac{1}{2} \mathbf{H}^2 + \frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} i_{\alpha}^s i_{\beta}^s \right) + \sum_{\alpha\beta} \sigma_{\alpha\beta} \mathbf{E}_{\alpha} \mathbf{E}_{\beta} + c \text{div } [\mathbf{E} \times \mathbf{H}] = 0 \quad (5-5)$$

In a superconductor there is, in addition to the electric and magnetic energy, a specific energy of the supercurrent having a density

$$\frac{1}{2} \sum_{\alpha\beta} \lambda_{\alpha\beta} i_{\alpha}^s i_{\beta}^s = \frac{1}{2} (\mathbf{i}^s \cdot \mathbf{G}) \quad (5-6)$$

or, for the cubic case

$$\frac{1}{2} \lambda \mathbf{i}^s{}^2 \quad (5-7)$$

This is the only difference from the older theory. If we wish to combine the laws of conservation, eqs. 5-3 and 5-5, which will be useful later, we put

$$\frac{1}{2} \epsilon \mathbf{E}^2 + \frac{1}{2} \mu \mathbf{H}^2 + \frac{1}{2} (\mathbf{i}^s \cdot \mathbf{G}) \quad (5-8)$$

for the total energy density. Our assumptions in Chap. 3 (b) about the tensors λ and σ ensure that the two sums in eq. 5-5 are always positive. Therefore it follows from eq. 5-5 that the energy of any electric field will be entirely dissipated by Joule heat if energy is not supplied from outside. Therefore if the superconductor does contain space charges, they must vanish. For if they were assumed to remain, there would exist an electric field without a magnetic field strength: the Poynting vector would be zero, and according to eq. 5-5 the field energy would decrease until the field and therefore also its charges become zero, contradicting the hypothesis. The conclusion drawn in Chap. 4 about the decay of the total space charge density ρ in superconductors with a cubic lattice structure is in this way applicable to all superconductors.

Stationary magnetic fields are, however, possible in which a supercurrent appears but no electric field strength. In deriving the energy law,

eq. 5-5, it is assumed that the $\lambda_{\alpha\beta}$ do not change with time, just as in eq. 5-2, ϵ and μ have to be constant. All these constants of the material depend on temperature. Therefore eqs. 5-2 and 5-5 can be used for isothermal processes only. The kinds of energy appearing here are therefore free energies in the sense of thermodynamics. The actual energy E is connected with the free energy F ¹ by the relation $E = F - T \partial F / \partial T$. Consequently the energy of the supercurrent per unit volume is

$$\frac{1}{2} \sum_{\alpha\beta} \left(\lambda_{\alpha\beta} - T \frac{\partial \lambda_{\alpha\beta}}{\partial T} \right) \mathbf{i}_{\alpha} \cdot \mathbf{i}_{\beta}$$

or for the cubic case

$$\frac{1}{2} \left(\lambda - T \frac{\partial \lambda}{\partial T} \right) \mathbf{i}^2$$

Reversing signs, the second terms, i. e., the expressions

$$\frac{1}{2} T \sum_{\alpha\beta} \frac{\partial \lambda_{\alpha\beta}}{\partial T} \mathbf{i}_{\alpha} \cdot \mathbf{i}_{\beta} \quad \text{or} \quad \frac{1}{2} T \frac{\partial \lambda}{\partial T} \mathbf{i}^2$$

represent the heat which has to be removed from the superconductor during isothermal production of the supercurrent \mathbf{i} . As λ increases with T they are positive, and immediately below the transition temperature they are quite considerable.

CHAPTER 6

The Telegrapher's Equation for Superconductors with Cubic Crystal Structure

It is known that by eliminating all field vectors but one from among Maxwell's field equations one obtains a partial differential equation for the remaining vector, the so-called telegrapher's equation which occupies a position intermediate between the wave equation $\Delta u - (1/c^2) \partial^2 u / \partial t^2 = 0$ and the equation for heat conduction $\Delta u - k^2 \partial u / \partial t = 0$. We now wish to perform this elimination for the superconductivity theory. We assume all constants of the material to be unvarying in time and space. The lattice shall be cubic. We form the curl of \mathbf{II} . Then from the rule

$$\text{curl curl } \mathbf{P} = \text{grad div } \mathbf{P} - \Delta \mathbf{P} \quad (6-1)$$

¹This is the Helmholtz free energy $F = E - TS$, not the Gibbs free energy $G = E - TS + PV + HM$.

and according to III, we obtain $-\Delta \mathbf{H}$ on the left-hand side. The result is therefore:

$$-\Delta \mathbf{H} = \frac{1}{c} \left\{ \text{curl} \frac{\partial \mathbf{E}}{\partial t} + \text{curl} \mathbf{i}^0 + \text{curl} \mathbf{i} \right\}$$

We transform the right-hand side of this by means of eqs. I, VII, and IX; the first term yields $-(1/c^2) \partial^2 \mathbf{H} / \partial t^2$, the second $-(\sigma/c^2) \partial \mathbf{H} / \partial t$, and the third $-\mathbf{H}/c^2 \lambda$. Consequently

$$W(\mathbf{H}) \equiv \Delta \mathbf{H} - \frac{1}{c^2} \frac{\partial^2 \mathbf{H}}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial \mathbf{H}}{\partial t} - \frac{\mathbf{H}}{c^2 \lambda} = 0 \quad (6-2)$$

Now we form the curl of eq. I, Because of IV, with $\rho = 0$ the only term we get on the left-hand side is $-\Delta \mathbf{E}$. By using eqs. II, and VII, then eqs. VIII and IX we reduce the right-hand side to

$$\begin{aligned} -\frac{1}{c} \text{curl} \frac{\partial \mathbf{H}}{\partial t} &= -\frac{1}{c^2} \left(\frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{\partial \mathbf{i}^0}{\partial t} + \frac{\partial \mathbf{i}}{\partial t} \right) \\ &= -\frac{1}{c^2} \left(\frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\lambda} \right) \end{aligned}$$

Consequently

$$W(\mathbf{E}) \equiv \Delta \mathbf{E} - \frac{1}{c^2} \left(\frac{\partial^2 \mathbf{E}}{\partial t^2} + \sigma \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{E}}{\lambda} \right) = 0 \quad (6-3)$$

If we again form the curl of eq. 6-2 it follows because of eq. II, and because the operator W can be interchanged with the operation of forming the curl:

$$W \left(\frac{\partial \mathbf{E}}{\partial t} + \mathbf{i} \right) = 0$$

By combining this with eq. 6-3 differentiated with respect to t , one gets

$$W(\mathbf{i}) = 0$$

On the other hand, multiplying eq. 6-3 by σ and using eq. VII give

$$W(\mathbf{i}^0) = 0 \quad (6-4)$$

Consequently by subtracting the last two equations, one finds from eq. V

$$W(\mathbf{i}^*) = 0 \quad (6-5)$$

The generalized telegrapher's equation $W(u) = 0$ therefore holds for each component of any of the field vectors with respect to cartesian coordinates. If the vectors were resolved in terms of curvilinear coordinates special treatment would be necessary.

Most experiments with superconductivity deal with stationary fields, so that their study constitutes the most important part of the theory. For

this case the equation for $W(u)$ is reduced to its first and its last terms: we are left with the differential equation

$$\Delta u - \beta^2 u = 0 \quad (6-6)$$

where u , as stated, represents a component of any field vector and where

$$\beta^2 = \frac{1}{c^2 \lambda} \quad (6-7)$$

Chaps. 7 and 11 will deal with this differential equation.

All the above is expressed in Lorentz units. In electrostatic units the last two terms in eq. 6-1 gain a factor 4π . So in place of eq. 6-7

$$\beta^2 = \frac{4\pi}{c^2 \lambda} \quad (\text{in esu}) \quad (6-8)$$

According to eq. 3-11 β has the same value in both systems of units.

CHAPTER 7

Stationary Fields

(a) As mentioned in Chap. 4 it follows from eq. IX that $\mathbf{E} = 0$ in the stationary case. Furthermore by eq. I, \mathbf{E} is the gradient of a scalar potential and so the superconductor is a region of constant potential even when the tensor components $\lambda_{\alpha\beta}$ vary with position in space. By eq. VII there is no ohmic current; it is deprived of its potential gradient by the presence of the supercurrent, i. e., it is short circuited. Therefore no experiment using direct current can enable us to detect the finite conductivity of the superconductor. The only significant field vectors are the current \mathbf{i} and the magnetic field \mathbf{H} . These vectors are more strongly coupled than in the normal conductor, because there exists between them not only the generally valid relation II, which here simplifies to

$$\text{curl } \mathbf{H} = \frac{\mathbf{i}}{c} \quad (7-1)$$

but also eq. IX applying specifically to superconductors:

$$\text{curl } \mathbf{G} = -\frac{\mathbf{H}}{c}, \quad \left(\mathbf{G}_\alpha = \sum_\beta \lambda_{\alpha\beta} i_\beta \right) \quad (7-2)$$

Everything we can say about the stationary case is based on the combined application of these two laws. This excludes the possibility of a current-free magnetic-potential field in a normal conductor. From $\text{curl } \mathbf{H} = 0$ it follows that $\mathbf{i} = 0$, $\mathbf{G} = 0$, and $\mathbf{H} = 0$. Strictly speaking there is no

outside field into which one could place a superconductor carrying a current. The current distribution changes with any attempt to do so in such a way as to annul the outside field. It is possible to keep the current strength constant, and if one considers only the total current strength, one may use the term "external field". In the following sections we shall follow this through for the superconductor with cubic crystal structure.

In many of the examples to be considered the field inside the superconductor is desired when the field in the surrounding space is known. It follows from a general theorem that the solution is unique. In fact, if we form the scalar product of eq. 7-1 with \mathbf{G} and of eq. 7-2 with $(-\mathbf{H})$, add the two, and apply the rule 5-1, we obtain

$$\text{div } [\mathbf{H} \times \mathbf{G}] = \frac{1}{c} \{ (\mathbf{i} \cdot \mathbf{G}) + \mathbf{H}^2 \} \quad (7-3)$$

Integrating eq. 7-3 over the volume of the superconductor and using Gauss' theorem¹

$$\int_S \text{div } [\mathbf{H} \times \mathbf{G}] d\tau = - \int_S [\mathbf{H} \times \mathbf{G}]_{n_i} d\sigma$$

we get

$$\frac{1}{c} \int_S \{ (\mathbf{i} \cdot \mathbf{G}) + \mathbf{H}^2 \} d\tau = \int_S [\mathbf{G} \times \mathbf{H}]_{n_i} d\sigma \quad (7-4)$$

The suffix S below the integral signs indicates that the volume integral extends over the volume of the superconductor and the surface integral over its entire surface.²

Now the normal component of the vector product $[\mathbf{G} \times \mathbf{H}]$ contains only the tangential components of \mathbf{G} and \mathbf{H} . If either $\mathbf{G}_t = 0$ or $\mathbf{H}_t = 0$ over the whole surface, then the right side of eq. 7-4 is zero. The left side, however, vanishes only if $\mathbf{H} = 0$ and $\mathbf{G} = 0$ or $\mathbf{i} = 0$ at every point of the superconductor.

Consider two fields $\mathbf{H}^{(1)}$, $\mathbf{i}^{(1)}$ and $\mathbf{H}^{(2)}$, $\mathbf{i}^{(2)}$ which coincide everywhere over the boundary either with respect to \mathbf{H}_{tang} or to \mathbf{G}_{tang} . Equation 7-4

¹ n_i indicates the inner normal on the surface $d\sigma$.

² If one uses the Gauss theorem for multiply connected regions, as we do later in Chap. 12, it is first necessary to produce singly connected regions by making a sufficient number of cuts and adding the new cross sections to the surface. Sometimes the cross sections make appreciable contributions. Here this is not the case because \mathbf{G} and \mathbf{H} are singlevalued functions of position, so that the contributions from both sides of any cross section cancel each other. Equation 7-4 therefore holds also for multiply connected superconductors.

³ According to eq. 3-4, $(\mathbf{i} \cdot \mathbf{G})$ is necessarily positive with the exception of the case where $\mathbf{i} = 0$, $\mathbf{G} = 0$.

holds equally well for the difference field $\mathbf{H}' = \mathbf{H}^{(1)} - \mathbf{H}^{(2)}$; $\mathbf{i}' = \mathbf{i}^{(1)} - \mathbf{i}^{(2)}$ because all our differential equations are linear; it follows then that the difference field vanishes throughout the volume: $\mathbf{H}' = 0$, $\mathbf{i}' = 0$. The stationary field in a superconductor is therefore uniquely determined by the tangential components at its surface of either the magnetic field or of the electromagnetic momentum of the supercurrents. This corresponds with the theorem of potential theory according to which the potential gradient in a region is uniquely fixed by its tangential components over the surface; these fix the surface potential to within an additive constant, and this in turn fixes the potential in the interior. The vectors \mathbf{G} and \mathbf{H} on the right-hand side of eq. 7-4 here refer to the inner side of the surface. It is also possible here to insert for \mathbf{H} its value on the outside of the surface because by Chap. 3 (c) the tangential component of \mathbf{H} is continuous across the surface. In this way the field in the interior is uniquely determined by the external magnetic field.

(b) For the homogeneous superconductor with a cubic lattice, eq. 7-2 can be simplified to read

$$\lambda \operatorname{curl} \mathbf{i}' = -\frac{1}{c} \mathbf{H} \quad (7-5)$$

If we form the curl of eq. 7-1, then the fundamental eq. III, and eq. 7-5 together with the theorem 6-1 give us

$$\Delta \mathbf{H} - \beta^2 \mathbf{H} = 0, \quad \beta^2 = \frac{1}{c^2 \lambda} \quad (7-6)$$

Conversely, if we form the curl of eq. 7-5, then use eqs. VI and 7-1, we get

$$\Delta \mathbf{i}' - \beta^2 \mathbf{i}' = 0 \quad (7-7)$$

Thus we come back at once to eqs. 6-6 and 6-7.

(c) The simplest conceivable example is that of a superconductor filling one half of space $z > 0$, so having the plane $z = 0$ as its boundary. If in outside space $z < 0$, there is a homogeneous magnetic field \mathbf{H}^0 , then eq. 6-6 can be solved by putting

$$\mathbf{H} = \mathbf{H}^0 e^{-\beta z} \quad (7-8)$$

Because $\operatorname{div} \mathbf{H} = 0$, \mathbf{H}_z^0 must be zero. We can turn the x and the (perpendicular) y directions in such a manner that \mathbf{H}_x^0 also vanishes. Then it follows that for the field strength in the superconductor

$$\mathbf{H}_x = \mathbf{H}_y = 0, \quad \mathbf{H}_z = H^0 e^{-\beta z} \quad (7-9)$$

Therefore according to eq. 7-1 the equations⁴

$$\mathbf{i}_x = -c \frac{\partial \mathbf{H}_y}{\partial z} = \beta c H^0 e^{-\beta z} = \lambda^{-1/2} H^0 e^{-\beta z}; \quad (7-10)$$

$$\mathbf{i}_y = \mathbf{i}_z = 0$$

⁴ In electrostatic units $\mathbf{i}_x = H^0 e^{-\beta z} / \sqrt{4\pi\lambda}$, compare eqs. 3-10 and 3-12.

represent the supercurrent vector field. We gather from this that the current density at the surface depends only on the field strength H^0 there.. \mathbf{i} , \mathbf{H} , and the inner normal of the superconductor are perpendicular to each other and form a right-handed system like the coordinate system x, y, z adopted here. The field penetrates the superconductor only to a depth of the order of magnitude β^{-1} . It forms a protecting layer of that thickness under which lies a region protected from the influence of the field. This result is fundamental because it can be taken over for the case of curved surfaces provided only that the superconductor is thick compared with the penetration depth β^{-1} . In this lies the explanation of the Meissner effect.

The surface density of the current is

$$\mathbf{i}_s = \int_0^\infty \mathbf{i}_x dz = c H^0 \quad (7-11)$$

In electrostatic units eq. 7-11 reads, by eq. 3-10

$$\mathbf{i}_s = \frac{c H^0}{4\pi}$$

and if the current is measured in amperes, $\mathbf{i}_s = 10 H^0 / 4\pi$: nearly 80 amp are flowing per centimeter across each magnetic line of force at $H^0 = 100$ oersteds. The penetration depth is

$$\beta^{-1} = c \sqrt{\lambda} \quad (7-12)$$

or $\beta^{-1} = c \sqrt{\lambda / 4\pi}$ in electrostatic units, by eq. 7-6. It is of the order of magnitude 10^{-5} cm if we assume for λ the order of magnitude 10^{-21} sec^2 , which is correct, according to present knowledge, for temperatures $\frac{1}{2} T_0$ or more below the transition temperature. Approaching the transition temperature T_0 , it appears to increase like λ without limit.

(d) We now consider the field and current distribution in thin superconductors, i. e., those with thickness no longer great compared with the penetration depth. We first treat the example of a plane parallel slab extending from $z = -d$ to $z = +d$. In the outside space let there be homogeneous magnetic fields H^- where $z < -d$ and H^+ where $z > d$, both in the y direction. The differential equation $\Delta \mathbf{H} - \beta^2 \mathbf{H} = 0$ and the condition $\operatorname{div} \mathbf{H} = 0$ are satisfied by

$$\mathbf{H}_x = \mathbf{H}_z = 0, \quad \mathbf{H}_y = a \cosh(\beta z) + b \sinh(\beta z) \quad (7-13)$$

It follows from eq. 7-1 that the current density is

$$\mathbf{i}_y = \mathbf{i}_x = 0, \quad \mathbf{i}_z = -c \frac{\partial \mathbf{H}_y}{\partial z} = -\lambda^{-1/2} \{a \sinh(\beta z) + b \cosh(\beta z)\} \quad (7-14)$$

The boundary condition that H_y be continuous at $z = \pm d$ yields two equations for the constants a and b :

$$a \cosh(\beta d) + b \sinh(\beta d) = H^+, \quad a \cosh(\beta d) - b \sinh(\beta d) = H^- \quad (7-15)$$

The solution of these is

$$a = \frac{(H^+ + H^-)}{2 \cosh(\beta d)}, \quad b = \frac{(H^+ - H^-)}{2 \sinh(\beta d)} \quad (7-16)$$

If $\beta d \gg 1$ there exists a protected region free from field and current between two protecting layers of thickness $1/\beta$. If $\beta d \ll 1$, by expanding eqs. 7-13, 7-14, and 7-16 in series we find to a first approximation

$$H_y = \frac{1}{2}(H^+ + H^-) + \frac{1}{2} \frac{(H^+ - H^-)z}{d}, \quad i_x = c \frac{(H^- - H^+)}{2d} \quad (7-17)$$

A surface current density

$$i_s = 2d i_x = c(H^- - H^+)$$

is therefore evenly distributed over the slab, the magnetic field increases linearly with z if the field strengths differ on the two sides of the slab. If, however, $H^+ = H^-$, no current flows, and the field is constant. If in a homogeneous magnetic field we place a sufficiently thin superconducting sheet parallel to the field strength, the field penetrates the sheet without being disturbed. For arbitrary thickness, but with $H^+ = H^-$, eqs. 7-13 and 7-14 simplify to

$$H_y = H^+ \frac{\cosh(\beta z)}{\cosh(\beta d)}, \quad i_x = -H^+ \frac{\sinh(\beta z)}{\sqrt{\lambda} \cosh(\beta d)} \quad (7-18)^5$$

(c) Consider now the same slab with a surface current density⁶ i_s with no magnetic field other than that produced by i_s . The current density is certainly an even function of z as the positive and negative z directions are equivalent, and we therefore need those solutions of the fundamental eqs. 7-14 for which $a = -b$. Also by eq. 7-13 H_y is an odd function of z , and consequently $H^- = -H^+$. Thus by eq. 7-15

$$b = \frac{H^+}{\sinh(\beta d)}$$

$$i_x = -H^+ \frac{\cosh(\beta z)}{\sqrt{\lambda} \sinh(\beta d)}, \quad H_y = H^+ \frac{\sinh(\beta z)}{\sinh(\beta d)} \quad (7-19)$$

and

$$u_P = \frac{\bar{u} \beta r}{\sinh(\beta r)} \quad (7-25)$$

The factor multiplying \bar{u} decreases from 1 to arbitrary small values with increasing r . For $\beta = 0$ it would always be 1, and eq. 7-25 would go over into the well-known mean value theorem of potential theory, according to which the function \bar{u} cannot have either a maximum or a minimum at any point P . However here, with $\beta > 0$, the equation says only that the absolute value $|u_P|$ is smaller than the absolute value $|\bar{u}|$, excluding a maximum of $|\bar{u}|$ at P , but certainly permitting a minimum. The highest values of $|u|$ never lie in the interior, but always on the boundary of the region in which the differential eq. 7-23 holds; for points on the surface it is not possible to construct such spheres so that eq. 7-25 does not apply.

Now we still have to calculate H^+ from i_s . The equation

$$i_s = \int_{-d}^d i_x dz = -2cH^+ \quad (7-20)$$

will serve for this. So the final result reads

$$i_x = \frac{1}{2} \beta i_s \frac{\cosh(\beta z)}{\sinh(\beta d)}, \quad H_y = -i_s \frac{\sinh(\beta z)}{2c \sinh(\beta d)} \quad (7-21)$$

For a thick slab ($\beta d \gg 1$) one finds again that the field and current are concentrated in two protecting layers adjacent to the boundary surface. For thin sheets ($\beta d \ll 1$), eq. 7-21 simplifies to

$$i_x = \frac{i_s}{2d}, \quad H_y = \frac{i_s z}{2cd} \quad (7-22)$$

The current is therefore evenly distributed through the thickness of the sheet.

(f) To generalize the results obtained from these examples a mean value theorem for scalar space functions u that obey the differential equation

$$\Delta u - \beta^2 u = 0 \quad (7-23)$$

proves to be useful. We describe a sphere of radius r around an arbitrary point P in the three-dimensional domain of the function and form the mean value over its surface satisfying the equation

$$\Delta \bar{u} - \beta^2 \bar{u} = 0 \quad (7-24)$$

Since however \bar{u} depends only on r

$$\Delta \bar{u} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{d\bar{u}}{dr} \right)$$

and the differential eq. 7-24 has the solutions

$$\bar{u} = \text{const.} \frac{\sinh(\beta r)}{\beta r} \quad \text{and} \quad \bar{u} = \text{const.} \frac{\cosh(\beta r)}{\beta r}$$

The second of these must be rejected because it increases without limit at $r = 0$. If we go to $r = 0$ in the first one, we see that the constant must be u_P , therefore we find

The components \mathbf{H}_x , \mathbf{H}_y , and \mathbf{H}_z of the magnetic field strength satisfy the differential eq. 7-23; therefore we find according to this theorem that

$$(\mathbf{H}_x^2)_P < (\overline{\mathbf{H}_x^2})^2$$

However, the mean square fluctuation over the surface of the sphere,

$$\frac{1}{4\pi r^2} \int (\mathbf{H}_x - \overline{\mathbf{H}_x})^2 |d\sigma| = \frac{1}{4\pi r^2} \int \mathbf{H}_x^2 |d\sigma| - (\overline{\mathbf{H}_x})^2 = \overline{\mathbf{H}_x^2} - (\overline{\mathbf{H}_x})^2$$

is necessarily positive; therefore *a fortiori*

$$(\mathbf{H}_x^2)_P < \overline{\mathbf{H}_x^2}$$

Since corresponding relations hold for \mathbf{H}_y and \mathbf{H}_z , we find by summation

$$(\mathbf{H}^2)_P < \overline{\mathbf{H}^2}$$

One can prove in the same manner that

$$(\dot{\mathbf{r}}^2)_P < (\overline{\dot{\mathbf{r}}^2})^2$$

There exists no maximum of the magnetic field strength or the current density in the interior of a superconductor. The highest values of \mathbf{H}^2 and $\dot{\mathbf{r}}^2$ are always located at the surface. The possibility of minima is demonstrated by the examples in sections (d) and (e) and also by those in the following paragraphs. This is the general theory of the Meissner effect.

If u depends only on two coordinates, the mean value is formed over a circle with radius r around the point P . Then

$$\Delta \bar{u} = \frac{1}{r} \frac{d}{dr} \left(r \frac{d\bar{u}}{dr} \right)$$

and eq. 7-25 is replaced by

$$u_P = \frac{\bar{u}}{I_0(\beta r)} \quad (7-26)^7$$

where $I_0(x)$ is the Bessel function of zero order to be discussed in more detail in Chap. 8. Since with increasing r , $I_0(\beta r)$ increases continuously from 1 and finally exceeds all limits,⁸ all conclusions drawn from eq. 7-25 can be taken over in the two-dimensional case.

(g) However, there are limits to be set to the Meissner effect which can be derived from eq. 7-25 or 7-26. If the region where the differential eq. 7-23 holds is small compared with the penetration depth β^{-1} then $\beta r \ll 1$ and $u_P = u$, i. e., in such a region any solution of eq. 7-23 coincides with a solution of the potential equation $\Delta u = 0$. Then the Meissner effect becomes undetectable. Examples are contained in the approximations 7-17 and 7-22 for the thin sheet; as a matter of fact in this case $\dot{\mathbf{r}}_P$ and \mathbf{H}_P do satisfy the potential equation.

In an infinitely long straight cylinder of arbitrary but small cross section with its axis along the z direction, we can consider

$$\dot{\mathbf{r}}_P = \text{constant}$$

⁷ $\dot{\mathbf{r}}_P = \sqrt{-1}$.

⁸ Compare the series expansion of eq. 8-6.

as the first approximation, because in this way $\Delta \dot{\mathbf{r}} = 0$. The supercurrent is then distributed in exactly the same way as an ohmic current. If, keeping the current density $\dot{\mathbf{r}}$, constant, we decrease all the dimensions of the cross section by a factor a , then the magnetic field strength decreases at corresponding points like a because by Stokes' theorem it follows from eq. 11, for any surface lying entirely inside the conductor that

$$\int \mathbf{H} \cdot d\mathbf{s} = \frac{1}{c} \int \dot{\mathbf{r}} \cdot d\sigma$$

and the surface of integration decreases like a^2 while the circumference decreases like a . Equation IX shows that the ratio of curl $\dot{\mathbf{r}}$ to \mathbf{H} decreases like a . This justifies neglecting curl $\dot{\mathbf{r}}$ in eq. 7-23. We can take this result over without hesitation for a curved wire provided that the radius of curvature is great compared with the dimensions of the cross section.

On the other hand if we place a sufficiently small superconductor of arbitrary shape in a static magnetic field of strength H^0 , then the field continues unchanged through the superconductor because it obeys the differential equation $\Delta \mathbf{H} = 0$. As here \mathbf{H} is curl free, no current is produced on this approximation. This is not a contradiction of eq. 7-5 because if we integrate that equation over a surface lying entirely inside the superconductor and transform the integral on the left side to a line integral over the circumference by means of Stokes' theorem we get

$$c \int \dot{\mathbf{r}} \cdot d\mathbf{s} = - \int \mathbf{H} \cdot d\sigma \quad (7-28)$$

We apply this to two geometrically similar superconductors which may differ in their superconductivity constants λ_1 and λ_2 . Let L_1 and L_2 be corresponding linear intervals. We choose two corresponding surfaces in the superconductors; the integrals on the right-hand side of eq. 7-28 are then in the ratio $(L_1/L_2)^2$. Corresponding parts of the circumferences are then in the ratio L_1/L_2 . Consequently the ratio of the current density components $\dot{\mathbf{r}}_a$ at corresponding points of the two bodies is

$$\frac{\dot{\mathbf{r}}_{a1}}{\dot{\mathbf{r}}_{a2}} = \frac{\lambda_2 L_1}{\lambda_1 L_2} = \sqrt{\frac{\lambda_2}{\lambda_1} \frac{\beta_1}{\beta_2} \frac{L_1}{L_2}}$$

Therefore for every sufficiently small superconductor every component $\dot{\mathbf{r}}_a$ of $\dot{\mathbf{r}}$, $a = 1, 2, 3$, can be developed in a series the first term of which has the form

$$\dot{\mathbf{r}}_a = H^0 \tau_a \frac{\beta L}{\sqrt{\lambda}} \quad (7-29)$$

The quantities τ_a here are pure numbers, depending only on the relative positions and the shapes, but no longer on λ or the size of the specimen. Examples will be found in eqs. 10-2 and 11-12 as well as in the discussion following eq. 10-16.

These results do not hold without restriction for multiply connected superconductors because in this case there exist surfaces (see Chap. 12)

that extend partly outside the superconductor, in spite of the fact that their perimeters lie completely inside it. It is not then permissible to apply eq. 7-2 which is valid only for surfaces entirely within the superconductor. We shall see that in this case a persistent current, independent of H^0 , can be superposed on the currents obeying eq. 7-29.

(h) According to Chap. 3 the constant λ is a function of temperature. Immediately below the transition temperature it is very great, and so is the penetration depth $\beta^{-1} = c/\lambda$. (See eq. 7-6.) Every specimen is then "small" in the sense of the present considerations, the magnetic field penetrates it undisturbed. With decreasing temperature λ decreases, at first very rapidly indeed. This initiates the expulsion of the field — the Meissner effect. If the specimen is wrapped with a normally conducting induction coil, one can follow this process by means of the induced current; it decreases the flux of induction through the coil. Such experimental tests have often been carried out. In one instance Stark, Steiner, and Schoeneck⁹ observed a "paramagnetic" effect in the induced current, i. e., an effect that corresponds to an increase in flux of induction, which preceded the expulsion of the field. There is as yet no explanation for this. It would not help to ascribe to the superconductor a permeability μ deviating from 1. According to eq. 6-7 the former value $1/c^2 \lambda$, of β^2 merely acquires a factor μ . As the observations concern β , this would change the conversion from β to λ , but would offer no explanation of the induction experiments.¹⁰

(i) We shall try to apply some of the above results to superconductors with noncubic crystal structure and consider again the simplest case: the superconductor fills half of space, $x_3 > 0$, and at its surface there is a static homogeneous magnetic field H^0 the direction of which we again take as the x_2 axis. The boundary conditions for $x_3 = 0$ are therefore

$$\mathbf{H}_1 = 0, \quad \mathbf{H}_2 = H^0 \quad (7-30)$$

The other boundary condition is again the gradual vanishing of all field vectors as x_3 increases toward infinity. The Maxwell eq. II, ($\text{curl } \mathbf{H} = \mathbf{i}/c$)

⁹J. Stark, K. Steiner, and H. Schoeneck, *Phys. Z.*, 88, 887 (1937).

¹⁰Another discrepancy with the theory appeared sometimes in such experiments in that the total induced current impulse seemed to be less, occasionally even much less, than would be consistent with the complete expulsion of the field. The objection to these measurements is that the whole specimen had actually not become superconducting, but only a ring-shaped outer part of it. The cooling is effected from outside, so once such a ring is formed, it holds the enclosed flux of induction constant, as described in detail in Chap. 12, no matter how the external field is changed. The other parts remain in the intermediate state due to the influence of the field. In the superconducting ring a persistent current is produced by switching off the field, (Chap. 12). A test for this would consist in looking for the magnetic field of such a persistent current after the external field has been switched off, but it seems that this test has never been made in such experiments.

and the London eq. X ($c \text{ curl } \mathbf{G} = -\mathbf{H}$) reduce according to eq. VIII to the following:

$$\mathbf{i}_1' = -c \frac{\partial \mathbf{H}_2}{\partial x_3}, \quad \mathbf{i}_2' = c \frac{\partial \mathbf{H}_1}{\partial x_3} \quad (7-31)$$

$$\mathbf{H}_1 = c \frac{\partial \mathbf{G}_2}{\partial x_3} = c \left(\lambda_{21} \frac{\partial \mathbf{i}_1'}{\partial x_3} + \lambda_{22} \frac{\partial \mathbf{i}_2'}{\partial x_3} \right) \quad (7-32)$$

$$\mathbf{H}_2 = -c \frac{\partial \mathbf{G}_1}{\partial x_3} = -c \left(\lambda_{11} \frac{\partial \mathbf{i}_1'}{\partial x_3} + \lambda_{12} \frac{\partial \mathbf{i}_2'}{\partial x_3} \right)$$

Because of the divergence conditions \mathbf{i}_3' and \mathbf{H}_3 vanish. Elimination of \mathbf{i}_1' leads to the differential equations

$$\begin{aligned} \lambda_{22} \frac{\partial^2 \mathbf{H}_1}{\partial x_3^2} - \lambda_{21} \frac{\partial^2 \mathbf{H}_2}{\partial x_3^2} - \frac{\mathbf{H}_1}{c^2} &= 0 \\ -\lambda_{12} \frac{\partial^2 \mathbf{H}_1}{\partial x_3^2} + \lambda_{11} \frac{\partial^2 \mathbf{H}_2}{\partial x_3^2} - \frac{\mathbf{H}_2}{c^2} &= 0 \end{aligned} \quad (7-33)$$

which here replaces eq. 7-6. The most obvious way to solve these is by introducing a new coordinate system x_1' and x_2' rotated about the x_3 axis, in which the tensor component λ_{12}' vanishes. These are the "relative" principal axes of the tensor (i. e., relative to the plane $x_3 = 0$), the principal axes of the ellipse formed by the intersection of this plane and the ellipsoid of the tensor: $\Sigma \lambda_{\alpha\beta} x_\alpha x_\beta = \text{constant}$. This ellipse gives the

"relative principal values" Λ_1' and Λ_2' of the tensor. Introducing these changes in eq. 7-33 yields at once the two solutions:

$$\begin{aligned} (1) \quad \mathbf{H}_1' &= H_1^0 e^{-\beta_1' x_3}, & \mathbf{H}_2' &= 0 \\ \mathbf{i}_1' &= 0, & \mathbf{i}_2' &= -H_1^0 e^{-\beta_1' x_3} / \Lambda_2' \\ \mathbf{G}_1' &= 0, & \mathbf{G}_2' &= -\Lambda_2' H_1^0 e^{-\beta_1' x_3} \end{aligned} \quad (7-34)$$

$$\begin{aligned} (2) \quad \mathbf{H}_1' &= 0, & \mathbf{H}_2' &= H_2^0 e^{-\beta_2' x_3} \\ \mathbf{i}_1' &= H_2^0 e^{-\beta_2' x_3} / \Lambda_1', & \mathbf{i}_2' &= 0 \\ \mathbf{G}_1' &= \Lambda_1' H_2^0 e^{-\beta_2' x_3}, & \mathbf{G}_2' &= 0 \end{aligned} \quad \begin{aligned} (\beta_2' &= 1/c \sqrt{\Lambda_2'}) \\ (\beta_1' &= 1/c \sqrt{\Lambda_1'}) \end{aligned} \quad (7-35)$$

The integration constants H_1^0 and H_2^0 are the external magnetic field strength components in the directions x_1' and x_2' respectively. However, the boundary condition 7-30 must hold with respect to the coordinates x_1 and x_2 . Denoting the angle between x_1 and x_1' by φ , as in Fig. 7-1, we have to put $H_2^0 = H^0 \cos \varphi$; $H_1^0 = -H^0 \sin \varphi$. Finally transforming the vector components of eqs. 7-34 and 7-35 back into the components with respect to x_1 and x_2 ,

$$\mathbf{H}_1 = \mathbf{H}_1' \cos \varphi + \mathbf{H}_2' \sin \varphi, \quad \mathbf{H}_2 = -\mathbf{H}_1' \sin \varphi + \mathbf{H}_2' \cos \varphi, \text{ etc.}$$

and we find

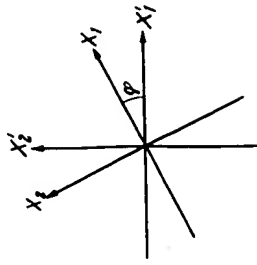


Fig. 7-1. Illustrating transformation of coordinates to principal axes.

$$\begin{aligned}
\mathbf{H}_1 &= H^0 \{ e^{-\beta_1' x_3} - e^{-\beta_1' x_3} \} \cos \varphi \sin \varphi \\
\mathbf{H}_2 &= H^0 \{ e^{-\beta_1' x_3} \cos^2 \varphi + e^{-\beta_1' x_3} \sin^2 \varphi \} \\
\mathbf{i}_1 &= H^0 \{ (1/\Lambda_1') e^{-\beta_1' x_3} \cos^2 \varphi + (1/\Lambda_2') e^{-\beta_1' x_3} \sin^2 \varphi \} \\
\mathbf{i}_2 &= -H^0 \{ (1/\Lambda_1') e^{-\beta_1' x_3} - (1/\Lambda_2') e^{-\beta_1' x_3} \} \cos \varphi \sin \varphi \\
\mathbf{G}_1 &= H^0 \{ \Lambda_1' e^{-\beta_1' x_3} \cos^2 \varphi + \Lambda_2' e^{-\beta_1' x_3} \sin^2 \varphi \} \\
\mathbf{G}_2 &= -H^0 \{ \Lambda_1' e^{-\beta_1' x_3} - \Lambda_2' e^{-\beta_1' x_3} \} \cos \varphi \sin \varphi
\end{aligned} \quad (7-36)^{11}$$

According to Chap. 3 (b), the relative principal values Λ_1' , Λ_2' are positive, therefore the decay constants β_1' and β_2' are certainly real. Because of the boundary condition at infinity, we must take them to be positive.

According to this, a noncubic crystal superconductor in a magnetic field also has a protecting layer under which exists a field-free region. In contrast to the case with a scalar λ , the decay does not follow one exponential function but two. Furthermore, the magnetic field strength in the protecting layer does not have the same direction x_3 everywhere, as in the outside space, nor does the current density have the same direction x_1 everywhere perpendicular to this. Neither does the scalar product $(\mathbf{i} \cdot \mathbf{H})$ vanish. However, the two parts of the energy density, that due to the supercurrent and that due to the magnetic field, remain equal to each other, because from eq. 7-36

$$\frac{1}{2} (\mathbf{i} \cdot \mathbf{G}) = \frac{1}{2} \mathbf{H}^0 \quad (7-37)$$

Also the total surface current $\int_0^\infty \mathbf{i} dx_3$ flows perpendicular to H^0 and its value is defined exclusively by H^0 through eq. 7-36:

$$\int_0^\infty \mathbf{i}_1 dx_3 = c H^0, \quad \int_0^\infty \mathbf{i}_2 dx_3 = 0 \quad (7-38)$$

This can of course be deduced directly from the Maxwell equations.

All these differences vanish either if the relative principal values Λ_1' and Λ_2' are equal, or if the external field coincides in direction with one of the relative principal axes, i. e., if $\varphi = 0$ or $\pi/2$. Then we return to one of the solutions 7-34 or 7-35.

One might also apply this solution to slightly curved conductors in so far as they are thick compared with the penetration depths $(\beta_1')^{-1}$ and $(\beta_2')^{-1}$, by considering the respective tangent planes as the x_3 plane.

For thin superconductors, however, the conditions are different. We see easily from eq. 7-33 that for a sufficiently thin plate the external magnetic field penetrates without hindrance and that a supercurrent is evenly distributed over it. From this we infer that the conclusions drawn in (f) for thin cubic crystal superconductors may also be applied to other lattices. As a confirmation of this we find in Chap. 8 (e) and Chap. 11 (f), that the solutions of London's equations, which lead to the above conclusions for cubic crystal cylinders and spheres, can under suitable conditions be applied to other crystal lattice forms.

¹¹ ϵ_3 is generally not zero but $\epsilon_3 = \lambda_{31} \mathbf{i}_1 + \lambda_{32} \mathbf{i}_2$.

CHAPTER 8

The Current Flowing in a Wire

(a) In sections (a) to (d) we shall discuss a circular cylinder of radius R carrying a current I in the direction of its axis, the z axis. We assume the current to be confined to a coaxial cylindrical shell so that we shall have a well-defined axially symmetrical external field. We assume the material of the superconductor to have a homogeneous cubic crystalline structure. We use cylindrical coordinates, the distance r from the axis, the azimuth angle θ measured from an arbitrary direction, forming a right-handed system with z in the order r, θ, z (compare Fig. 8-1).

In these coordinates the components of the vector curl are

$$\text{curl}_r \mathbf{A} = \frac{1}{r} \frac{\partial A_z}{\partial \theta} - \frac{\partial A_\theta}{\partial z}$$

$$\text{curl}_\theta \mathbf{A} = \frac{\partial A_r}{\partial z} - \frac{\partial A_z}{\partial r} \quad (8-1)$$

$$\text{curl}_z \mathbf{A} = \frac{1}{r} \frac{\partial(r A_\theta)}{\partial r} - \frac{1}{r} \frac{\partial A_r}{\partial \theta}$$

and for a scalar u :

$$\Delta u = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} + \frac{\partial^2 u}{\partial z^2} \quad (8-2)$$

In what follows we shall use solutions of the differential equation $\Delta u - \beta^2 u = 0$ of the form

$$u = f(r) e^{n\theta} e^{\pm k z} \quad (n \text{ an integer}) \quad (8-3)$$

Then $f(r)$ must satisfy the equation

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{df}{dr} \right) + \left(k^2 - \beta^2 - \frac{n^2}{r^2} \right) f = 0 \quad (8-4)$$

By the substitution $x = \sqrt{k^2 - \beta^2} r$ this is transformed into the Bessel equation

$$\frac{1}{x} \frac{d}{dx} \left(x \frac{df}{dx} \right) + \left(1 - \frac{n^2}{x^2} \right) f = 0 \quad (8-5)$$

The solutions of eq. 8-5 which remain finite for $x = 0$ are the Bessel functions $I_n(x)$, namely,



Fig. 8-1. Cylindrical coordinates r, θ for a wire. The z axis is directed toward the reader; A is the intersection of the z axis with the plane of the diagram.

$$\begin{aligned}
 I_0(x) &= 1 - \frac{(\frac{1}{2}x)^2}{(1!)^2} + \frac{(\frac{1}{2}x)^4}{(2!)^2} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m}}{(m!)^2} \dots \\
 I_1(x) &= \frac{\frac{1}{2}x}{0!1!} - \frac{(\frac{1}{2}x)^3}{1!2!} + \frac{(\frac{1}{2}x)^5}{2!3!} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m+1}}{m!(m+1)!} \dots \\
 I_2(x) &= \frac{(\frac{1}{2}x)^2}{0!2!} - \frac{(\frac{1}{2}x)^4}{1!3!} + \frac{(\frac{1}{2}x)^6}{2!4!} - \dots + \frac{(-1)^m (\frac{1}{2}x)^{2m}}{(m-1)!(m+1)!} \dots
 \end{aligned} \quad (8-6)$$

One may verify that these series satisfy the following equations:

$$\begin{aligned}
 \frac{dI_0(x)}{dx} &= -I_1(x) \\
 \frac{dI_1(x)}{dx} &= I_0(x) - \frac{1}{x} I_1(x) \\
 \frac{1}{x} \frac{d[x I_1(x)]}{dx} &= I_0(x) + I_2(x) = \frac{2}{x} I_1(x)
 \end{aligned} \quad (8-7)$$

For real arguments, x , the functions $I_n(x)$ oscillate about zero and have an infinity of roots. For pure imaginary arguments, the functions increase monotonically without limit with increasing argument.

(b) Let us consider an infinitely long homogeneous superconducting circular cylinder. By symmetry the current density is parallel to the axis and depends only on r . Therefore i_r must obey the differential eq. 8-4 with $n=0$ and $k=0$. The substitution used in the transition to eq. 8-5 is now $x = i\beta r$ and so

$$i_r = C I_0(i\beta r), \quad i_z = i_0 = 0 \quad (8-8)$$

The integration constant is determined by the condition that a total current I flows through the cross section. Consequently,

$$I = 2\pi \int_0^R r i_r dr = 2\pi C \int_0^R r I_0(i\beta r) dr = 2\pi \frac{C R}{\beta} [-i I_1(i\beta R)]$$

(see eq. 8-7). From this it follows that

$$C = \frac{(I \beta / 2\pi R)}{I_1(i\beta R)}, \quad i_r = \frac{i\beta I}{2\pi R} \frac{I_0(i\beta r)}{I_1(i\beta R)} \quad (8-9)$$

Since according to eq. 8-6 $I_0(i\beta r)$ is real and positive, while $I_1(i\beta r)$ is positive imaginary, the right sides of these equations are positive real.

The magnetic field strength is determined by the fundamental eq. X:

$$\mathbf{H} = -c \lambda \text{curl } \mathbf{i}$$

Therefore according to eq. 8-1

$$\mathbf{H}_r = \mathbf{H}_z = 0, \quad \mathbf{H}_\theta = c \lambda \frac{\partial i_r}{\partial r} = i c \lambda \beta C \left(\frac{dI_0(x)}{dx} \right)_{x=i\beta r} \quad (8-10)$$

that is by eqs. 8-7 and 6-7:

$$\mathbf{H}_\theta = \sqrt{\lambda C} [-i I_1(i\beta r)] = \frac{I}{2\pi c R} \frac{I_1(i\beta r)}{I_1(i\beta R)} \quad (8-11)$$

We can check this equation by setting $r = R$. At the surface of the cylinder carrying a total current I we must have

$$\mathbf{H}_\theta = \frac{I}{2\pi c R} \quad (8-12)$$

and this actually is the result.

The Bessel functions $I_0(i\beta x)$ and $I_1(i\beta x)$ increase toward infinity as e^x/\sqrt{x} . If βR is a high number, the wire therefore thick compared with the penetration depth, then according to eq. 8-9 with $\beta r \gg 1$, i_r contains the factor $e^{-\beta(R-r)}$. The current, and likewise the magnetic field, lie almost entirely in a protecting layer of thickness β^{-1} . On the other hand $I_0(i\beta x)$ has a minimum at $x=0$ (equal to 1), and if $\beta R \ll 1$, then the current density i_r increases only slightly from the axis to the perimeter — it is more or less evenly distributed over the section. Both results were to have been expected according to Chap. 7.

(c) Now let the cylinder consist of a normally conducting part where $z < 0$ and a superconducting part where $z > 0$. According to Chap. 7 the electrostatic potential is constant inside the superconductor. The boundary plane at $z=0$ is thus an equipotential surface for the normal conductor; therefore the current flows exactly as in a wire of unlimited length, namely, it is evenly distributed over the cross section. The current density is

$$i_r = \frac{I}{\pi R^2} \quad (z < 0)$$

The magnetic lines of force here are circles around the axis of the wire. Since $\int \mathbf{H}_\theta \cdot d\mathbf{s}$ integrated round a circle of radius $r < R$ must equal the total current through the circle, $I \cdot r^2/R^2$, divided by c , we have

$$\mathbf{H}_\theta = \frac{r \cdot I}{2\pi c R^2} \quad (z < 0) \quad (8-13)$$

On entering the superconductor the current must restrict itself to the boundary layers. We have therefore to take into account a radial component i_r in the neighborhood of the boundary plane. Because of this it is more expedient to start with the magnetic field strength which even at this point has by symmetry only a component \mathbf{H}_θ independent of θ . For large positive values of z we can use the solution 8-11 directly; in the neighborhood of $z=0$, however, other terms have to be added that decrease with increasing z .

As already mentioned, the differential equation $\Delta u - \beta^2 u = 0$ holds for \mathbf{H}_z and \mathbf{H}_r , but not for \mathbf{H}_θ which is associated with a curvilinear coordinate. Since, however,

$$\mathbf{H}_z = -\mathbf{H}_\theta \sin \theta, \quad \mathbf{H}_r = \mathbf{H}_\theta \cos \theta$$

we may write, using an a priori undetermined constant α_θ

$$\mathbf{H}_\theta = f(r) e^{-\sqrt{\alpha_\theta^2 + \beta^2} z}$$

so that we get

$$\mathbf{H}_r = i \mathbf{H}_z = f(r) e^{\theta} e^{-\sqrt{\alpha_\theta^2 + \beta^2} z}$$

Comparison with eq. 8-3 proves that $f(r)$ must be a solution of eq. 8-4 with $n = 1$ and $k = \sqrt{a_p^2 + \beta^2}$, i. e.,

$$f(r) = I_1(a_p r)$$

If we insert such additional terms in the solution 8-11 it becomes inconsistent with eq. 8-12, an equation which must still hold; we therefore determine a_p by the requirement that

$$I_1(a_p R) = 0 \quad (8-14)$$

As there are infinitely many zeros of $I_1(x)$, a discrete but infinite set of real a_p values satisfy this condition.

In this way we arrive at the following series for H_θ :

$$H_\theta = \frac{I}{2\pi c R} \left[\frac{I_1(\epsilon \beta r)}{I_1(\epsilon \beta R)} + \sum_{p=1}^{\infty} a_p I_1(a_p r) e^{-\sqrt{a_p^2 + \beta^2} z} \right] (z > 0) \quad (8-15)$$

and now have only the coefficients a_p to calculate. For this purpose the continuity condition for H_θ at $z = 0$ is available. Because of eq. 8-13

$$\sum_{p=1}^{\infty} a_p I_1(a_p r) = \frac{r}{R} - \frac{I_1(\epsilon \beta r)}{I_1(\epsilon \beta R)} \quad (8-16)$$

must hold identically in r . To carry out the calculations two relations are available which we accept without proof:

$$\begin{aligned} \int_0^R r I_1(\gamma r) I_1(\delta r) dr &= \frac{[\delta R I_1(\gamma R) I_0(\delta R) - \gamma R I_1(\delta R) I_0(\gamma R)]}{(\gamma^2 - \delta^2)} \\ \int_0^R r I_1^2(\gamma r) dr &= \frac{1}{2} R^2 [I_1^2(\gamma R) - I_0(\gamma R) I_2(\gamma R)] \end{aligned} \quad (8-17)$$

From the first of these follows the important fact that the functions $I_1(a_p r)$ selected by eq. 8-14 form an orthogonal system, i. e.,

$$\int_0^R r I_1(a_p r) I_1(a_q r) dr = 0 \quad \text{for } a_p \neq a_q$$

Multiplying eq. 8-16 by $r I_1(a_q r)$ and integrating from 0 to R therefore eliminates all the coefficients except a_q and yields for it the value

$$a_q = \frac{\int_0^R r \left[\frac{r}{R} - \frac{I_1(\epsilon \beta r)}{I_1(\epsilon \beta R)} \right] I_1(a_q r) dr}{\int_0^R r I_1^2(a_q r) dr}$$

The integration can be carried out easily by means of eqs. 8-7 and 8-17. The result is

$$a_q = -\frac{1}{2 a_q R} \left\{ \frac{1}{I_0(a_q R)} + \frac{a_q^2/(\alpha_q^2 + \beta^2)}{I_2(a_q R)} \right\}$$

Because of the last of the equations 8-7, eq. 8-14 is $I_2(a_q R) = -I_0(a_q R)$ so

$$a_q = -\frac{1}{2 a_q R} \frac{\beta^2/(\alpha_q^2 + \beta^2)}{I_0(a_q R)} \quad (8-18)$$

We get the current density now from the fundamental eq. II:

$$\mathbf{i} = c \operatorname{curl} \mathbf{H}$$

According to eqs. 8-1, 8-7, and 8-15 this yields

$$\begin{aligned} i_r &= -c \frac{\partial H_\theta}{\partial z} = \frac{I}{2\pi R} \sum_{p=1}^{\infty} a_p \left[\frac{1}{a_p^2 + \beta^2} I_1(a_p r) e^{-\sqrt{a_p^2 + \beta^2} z} \right. \\ i_r &= \frac{c}{r} d(r H_\theta)/dr \\ &= \frac{I}{2\pi R} \left[\frac{\epsilon \beta I_0(\epsilon \beta r)}{I_1(\epsilon \beta R)} + \sum_{p=1}^{\infty} a_p \alpha_p I_0(a_p r) e^{-\sqrt{a_p^2 + \beta^2} z} \right] \end{aligned} \quad (8-19)$$

Because of eq. 8-14 i_r vanishes at the surface of the cylinder $r = R$ as required. The same is true at $r = 0$ because $I_1(0) = 0$.

Furthermore, as soon as $\beta z \gg 1$, both i_r and that part of i_r represented by the sum over p vanish. Then i_r assumes the same value as for the infinitely long superconducting cylinder given in eq. 8-9. The transition from the even current distribution that still exists at the boundary $z = 0$ to the distribution that characterizes the superconductor is effected in a distance β^{-1} .

The first roots of eq. 8-14 are

$$a_1 R = 3.83, \quad a_2 R = 7.02, \quad a_3 R = 10.2, \quad a_4 R = 16.6 \dots$$

If therefore $\beta R \geq 100$ (with $\beta = 10^5 \text{ cm}^{-1}$, $R = 10^{-3} \text{ cm}$ is sufficient for this), these first a_q are all small compared with β . Then i_r is great compared with the contribution to i_r from the sum over p . But according to what has been said in section (b) about the exponential decay of the first terms, this contribution to i_r is practically the only one in the region where r is considerably smaller than R . So in this region the lines of flow, which leave the boundary of the normal conductor evenly distributed and perpendicular to the boundary, bend sharply into the radial direction. They have to do this because the major portion of the current must be deflected from the interior of the wire into the protecting layer of thickness β^{-1} adjoining the cylinder's surface, and do this within a distance of β^{-1} in the z direction.

The thinner the wire the greater become the a_q , and if $\beta R \ll 1$ they are considerably greater than β . According to eq. 8-18 the coefficients a_q then all decrease, and with them the sum in eq. 8-19, and so also the radial

current i_r . The latter is no longer needed because, according to (b) the current is uniformly distributed over the cross section even in the superconductor.

(d) Let the cylinder now consist of two superconductors touching in the plane $z = 0$. Let the poorer superconductor lie below this plane; $z < 0$, corresponding to the smaller constant λ' , and therefore to the greater reciprocal penetration depth β' . By section (b) the current distribution depends on β so transition phenomena must now appear on both sides of the boundary.

For $z > 0$ we can retain the expression 8-15 with the values of a_p given by eq. 8-14, and also the consequent eq. 8-19. For $z < 0$ we write down the analogous expression:

$$\mathbf{H}_\theta' = \frac{I}{2\pi c R} \left\{ \frac{I_1(\iota\beta r)}{I_1(\iota\beta R)} + \sum_{p=1}^{\infty} a_p' I_1(a_p r) e^{+\sqrt{a_p'^2 + \beta'^2} z} \right\} \quad (z < 0) \quad (8-20)$$

The resulting calculation of the current distribution differs from eq. 8-19 not only in the sign of the exponents but also in the sign of the right-hand side of the equations for i_r . We have two boundary conditions to evaluate the coefficients a_p and a_p' , first the continuity of \mathbf{H}_θ and second (see Chap. 3, eq. 3-9)

$$\lambda i_r = \lambda' i_r'$$

according to eq. 6-7 we can also write for this

$$\frac{i_r}{i_r'} = \frac{\beta^2}{\beta'^2} \quad (8-21)$$

This second condition is fulfilled identically in r only if the corresponding coefficients in the two series for i_r and i_r' are in the ratio β^2/β'^2 :

$$\frac{a_q}{a_q'} \sqrt{\frac{(a_q^2 + \beta^2)}{(a_q'^2 + \beta'^2)}} = -\frac{\beta^2}{\beta'^2}$$

or

$$a_q' = -a_q \left(\frac{\beta'}{\beta} \right)^2 \sqrt{\frac{(a_q^2 + \beta^2)}{(a_q'^2 + \beta'^2)}} \quad (8-22)$$

The continuity of \mathbf{H}_θ , however, requires that

$$\sum_{p=1}^{\infty} (a_p - a_p') I_1(a_p r) = \frac{I_1(\iota\beta' r)}{I_1(\iota\beta R)} - \frac{I_1(\iota\beta r)}{I_1(\iota\beta R)} \quad (8-23)$$

identically in r . Applying the method used in (b) we conclude:

$$a_q - a_q' = \frac{2a_q}{R I_0(a_q R)} \frac{\beta'^2 - \beta^2}{(a_q^2 + \beta^2)(a_q'^2 + \beta'^2)} \quad (8-24)$$

This equation and 8-22 determine both a_p and a_p' . We see that if we assume $\beta' = \beta$ all the a_p and the a_p' vanish, as indeed must be so.

The transformation from one current distribution to the other takes place in two layers adjoining the boundary plane $z = 0$ of thickness β^{-1}

and β'^{-1} respectively. It is effected by radial currents in both superconductors. To find the contributions of each of the two conductors, we

compare the integrals $\int_0^\infty i_r dz$ and $\int_{-\infty}^0 i_r dz$. As

$$i_r = -c \frac{\partial \mathbf{H}_\theta}{\partial z}$$

both yield the same value for $(\mathbf{H}_\theta)_{z=0}$. The greater absolute value of i_r , which according to eq. 8-21 occurs in the better superconductor, is compensated by the smaller depth of the boundary layer. In the three cases treated here the magnetic field outside the superconductor is known *a priori*. The solutions therefore come under the uniqueness theorem of Chap. 7 (a).

(e) The solutions of section (b), i. e., of the problem of the infinitely long cylinder carrying a current, can be applied to noncubic crystal superconductors only if one of the axes of the ellipsoid representing the tensor $\lambda_{\alpha\beta}$ coincides with the axis of the cylinder. We call this axis the x_3 axis. If i_r has this direction everywhere then by eq. VIII the supermomentum has only one component \mathbf{G}_3 . The only tensor component that enters the calculation is the principal value λ_3 . It is only necessary to replace β in eqs. 8-9 and 8-10 by

$$\beta_3 = \frac{1}{c \sqrt{\lambda_3}} \quad (8-25)$$

to take over the former solution. Its uniqueness is again guaranteed by the theorem of Chap. 7 (a).

(f) It has not yet been possible to give a rigorous solution of our problem for a cylinder with an elliptical cross section, except in the approximation corresponding to the "thick" cylinder. In this case the circumference of the surface is a line of force of the external magnetic field. This field is irrotational and its potential obeys the equation $\Delta \Phi = 0$, but it increases with each turn around the cylinder by the "period"

$$-\oint \mathbf{H} \cdot d\mathbf{s} = -\frac{I}{c}$$

where, as before, I means the total current in the cylinder. Let the axes of the elliptical cross section be a and b ($a > b$). The "thick" cylinder is characterized by the fact that the smallest radius of curvature b^2/a at the ends of the greater axis is great compared with the penetration depth β^{-1} . The same holds *a fortiori* for b .

It is well known that if a functional relation $\zeta = f(\chi)$ exists between two complex variables $\zeta = x + iy$ and $\chi = \psi + i\varphi$, then ψ and φ are solutions of the potential equation. In the present problem

$\zeta = C \cosh(\alpha \chi) = C [\cosh(\alpha \psi) \cos(\alpha \varphi) + i \sinh(\alpha \psi) \sin(\alpha \varphi)] \quad (8-26)$
can be adjusted to the given boundary conditions. The constants C and α are available for this purpose.

Thus it follows from eq. 8-26 that

$$x = C \cosh(a\psi) \cos(a\varphi), \quad y = C \sinh(a\psi) \sin(a\varphi) \quad (8-27)$$

Elimination of φ yields

$$\left[\frac{x}{\cosh(a\psi)} \right]^2 + \left[\frac{y}{\sinh(a\psi)} \right]^2 = C^2 \quad (8-28)$$

The curves $\psi = \text{constant}$ are everywhere orthogonal to the curves $\varphi = \text{constant}$ and so represent the lines of force. If we fix a value ψ_0 in such a way that

$$a = C \cosh(a\psi_0) \quad \text{and} \quad b = C \sinh(a\psi_0)$$

or

$$C^2 = a^2 - b^2, \quad \tanh(a\psi_0) = \frac{b}{a} \quad (8-29)$$

then the surface of the cylinder contains the corresponding line of force, as required by the one boundary condition. All the other lines of force are ellipses confocal with the cross section of the cylinder. The period of the potential has the prescribed value if we put

$$a = -\frac{2\pi c}{I} \quad (8-30)$$

The magnitude H of the field strength follows from the general equation

$$H = |d\chi/d\zeta|$$

according to eq. 8-26:

$$\begin{aligned} H &= \frac{1}{C|a| |\sinh(a\chi)|} \\ &= \frac{1}{\{C|a| [\sinh^2(a\psi) \cos^2(a\varphi) + \cosh^2(a\psi) \sin^2(a\varphi)]^{1/2}\}} \end{aligned} \quad (8-31)$$

In particular the field strength at the surface $\psi = \psi_0$ is (see eq. 8-29)

$$H^0 = \frac{I}{2\pi c} [a^2 \sin^2(a\varphi) + b^2 \cos^2(a\varphi)]^{-1/2} \quad (8-32)^1$$

Consequently at the end point of the greater axis ($y = 0$, $\sin(a\varphi) = 0$ by eq. 8-27), H^0 is a maximum exceeding the minimum at the end of

¹The transformation from φ to the polar angle $\theta = \arctan y/x$ can be effected by an equation following from eq. 8-27:

$$\tan \theta = \tanh(a\psi) \tan(a\varphi)$$

Applying this to eq. 8-32 we have to put $\tan \theta = (b/a) \tan(a\varphi)$ according to eq. 8-29. The result is

$$H^0 = \frac{I}{2\pi c} \sqrt{\frac{a^2 \sin^2 \theta + b^2 \cos^2 \theta}{a^4 \sin^2 \theta + b^4 \cos^2 \theta}}$$

the smaller axis [$x = 0$ and $\cos(a\varphi) = 0$] by the factor a/b . According to eq. 7-38 this statement is equally true of the surface density of the supercurrent, whatever the crystal structure of the conductor. If d is the perpendicular distance of an interior point from the surface, then according to eq. 7-10 for a cubic lattice, the current density within the protecting layer is

$$i_t = H^0 \lambda^{-1/2} e^{-\beta d} \quad (8-33)$$

and practically no current is flowing in the protected region beneath.

(g) The fact that the supercurrent prefers protruding edges is no peculiarity of the elliptical cylinder, but a general characteristic of this current. It is caused by the well-known fact that when the lines of force envelope the surface of a body, the field intensity is considerably increased at such edges. The potential theory proves this as follows.

If as in section (f) we start from the conformal mapping $\chi = -\epsilon C \zeta^n$ then ψ , the real part of χ , equals $C |\zeta|^n \sin(n\theta)$; we take n to be a fraction between $1/2$ and 1. The line of force $\psi = 0$ consists of the radial lines $\theta = 0$ and $\theta = \pi/n$. In our mapping we see the representation of a field whose lines of force run along the surface of the superconductor filling the space $\pi/n < \theta < 2\pi$. At the protruding edge $\zeta = 0$

$$H = \left| \frac{d\chi}{d\zeta} \right| = n C |\zeta|^{n-1}$$

becomes infinite. If the edge is not mathematically sharp, but rounded, H remains finite, but in any case becomes especially large compared with the surrounding field. If we choose $n > 1$ we get a re-entrant edge and see that H decreases to zero therein.

In a column with rectangular cross section the strongest current runs along the four edges.

However this holds only under the conditions for a "thick" superconductor, and this excludes mean radii of curvature comparable with or smaller than the penetration depth β^{-1} . In extremely thin superconductors the supercurrent is distributed evenly over the cross section in accordance with Chap. 7 (g).

$$\frac{dH_0(x)}{dx} = -H_1(x) \quad (9-4)$$

and is a solution of the differential eq. 8-5 with $n = 1$. $H_1(\iota y)$ is negative real everywhere, becoming infinite like $-2/(\pi y)$; it increases monotonically reaching the value zero only for infinitely large positive values of y . It now follows from eq. 8-3 as in eq. 8-10 that

$$H_0 = c\lambda \frac{\partial i_z}{\partial r} = \sqrt{\lambda} [C - \iota I_1(\iota\beta r) + D H_1(\iota\beta r)] \quad (9-5)$$

According to eqs. 9-1 and 9-2, the equations determining the constants C and D are

$$\begin{aligned} -\iota C I_1(\iota\beta R_i) + D H_1(\iota\beta R_i) &= \frac{\beta I'}{2\pi R_i} \\ -\iota C I_1(\iota\beta R_e) + D H_1(\iota\beta R_e) &= \frac{\beta(I + I')}{2\pi R_e} \end{aligned} \quad (9-6)$$

We need not write out the solution explicitly. For a thick hollow cylinder, i. e., when $R_e - R_i \gg \beta^{-1}$, the first terms in eqs. 9-3 and 9-5 decrease toward the interior and can be neglected completely in the neighborhood of R_i , and similarly the second terms decrease toward the outside and are negligible near R_e .

Then we have simply

$$C = \frac{(I + I')(\iota\beta/2\pi R_e)}{I_1(\iota\beta R_e)}, \quad D = \frac{I'(\beta/2\pi R_i)}{H_1(\iota\beta R_i)} \quad (9-7)$$

Comparing this value of C with that in eq. 8-9 we see that the outer protecting layer of the cylindrical shell now carries the current $I + I'$. The equation for D shows that the protecting layer adjoining the inner surface carries the current $-I'$ because $H_1(\iota\beta R_i)$ is negative and $\iota H_0(\iota\beta r)$ in eq. 9-3 is positive. (See Fig. 9-1.) And this must be so; because a circle $r = \text{constant}$ within the protected interior of the cylindrical shell must enclose zero net current because $\mathbf{H} = 0$ on the circle. This current $-I'$ on the inner wall of the shell must be compensated by an additional current $+I'$ in the outer surface in order to have the total current I for the whole cylinder. Also it is only in this way that we can satisfy at the inner wall the rule that the current, the magnetic field strength, and the inner normal to the superconductor form a right-handed system.

For thin hollow cylinders, $R_e - R_i \ll \beta^{-1}$, one develops the two cylinder functions of eq. 9-5 in powers of $r - R_m$ starting from $R_m = \frac{1}{2}(R_e + R_i)$. One sees without calculation that, to a first approximation there is a linear transition from one to the other of the two values of H_0 prescribed by eqs. 9-1 and 9-2. This corresponds to the linear transition in the thin plane parallel plate of Chap. 7, eq. 7-17.

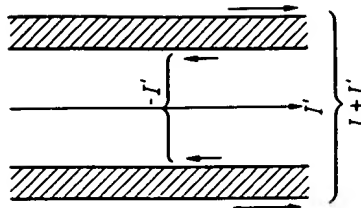


Fig. 9-1. Current distribution in a hollow superconducting cylinder with a coaxial wire. I is the net current in the superconducting cylinder; I' is the current in the coaxial wire.

The Current Flowing in a Hollow Cylinder

(a) For our present discussion let us consider a hollow cylinder with an inner radius R_i and outer radius R_e . Let the cylinder be homogeneous, superconducting, and have cubic crystal structure; let a total current I flow along it. But also let a wire, either normal or superconducting, be placed along the axis of the cylinder and carry another current I' . We consider I or I' to be positive if they flow in the positive z direction. We imagine the circuit to be closed by means of a coaxial cylindrical shell at infinity, as in Chap. 8.

Under these circumstances the magnetic field strength at the inner cylindrical surface $r = R_i$ is

$$H_\theta = \frac{I'}{2\pi c R_i} \quad (r = R_i) \quad (9-1)$$

because a circle of radius R_i encloses the current I' . A circle lying in the outer cylindrical surface ($r = R_e$), however, encloses the total current $I + I'$. Consequently the field strength there is

$$H_\theta = \frac{I + I'}{2\pi c R_e} \quad (r = R_e) \quad (9-2)$$

From these conditions we can obtain the fields within the cylinder uniquely according to the theorem of Chap. 7 (a).

The current is parallel to z and depends only on r just as for the solid cylinder [Chap. 8 (b)]. Furthermore i_z is again a solution of the differential equation $\Delta u - \beta^2 u = 0$. But eq. 8-8 is insufficient because we cannot satisfy both conditions 9-1 and 9-2 with only one integration constant. However, we are relieved of the requirement that i_z must remain finite for $r = 0$ because the domain of the desired solution does not extend so far. Therefore we can generalize the expression 8-8 as follows:

$$i_z = C I_0(\iota\beta r) + \iota D H_0(\iota\beta r) \quad (9-3)$$

where $H_0(x)$ is the Hankel function of the first kind¹ and zero order, namely, that solution of the differential eq. 8-5 with $n = 0$ which becomes logarithmically infinite at the origin; $I_0(x)$ also satisfies eq. 8-5. $H_0(x)$ is so defined that $\iota H_0(\iota y)$ is positive real for positive real y and behaves at $y = 0$ like $-(2/\pi) \ln y$; it decreases monotonically with increasing y , and finally vanishes asymptotically. The Hankel function of the first kind and first order $H_1(x)$ is connected with $H_0(x)$ by the relation

¹ We can omit the usual suffix 1 because we shall not have to deal with the Hankel function of the second kind.

The solution given in eqs. 9-6 and 9-7 can be generalized to non-cubic crystals as in Chap. 8 (e) if one principal axis of the tensor falls in the direction of the cylinder. One only has to replace β by the β_3 of eq. 8-25. Everything that follows in this chapter holds independently of all crystallographic properties.

As explained in Chap. 1 every "thick" superconductor (there have been scarcely any experiments done on thin hollow cylinders) can stand only a certain critical value H_c at its surface. According to eqs. 9-1 and 9-2 this sets a limit for the superconducting state of the hollow cylinder:

$$|I'| < 2\pi c R_i H_c, \quad |I + I'| < 2\pi c R_o H_c \quad (9-8)$$

If we plot I and I' as coordinates in a plane (Fig. 9-2) the interior of the shaded parallelogram represents the region of superconductivity. This simple consequence of the Silsbee hypothesis has never been checked experimentally in a rigorous manner.

(b) Figure 9-3 represents the cross section of an arrangement of normal and superconducting parts symmetrical with respect to the z axis. Leads in the z axis may supply the current I . We ask what part of I flows

through the inner solid cylinder, and what part flows through the outer hollow cylinder. This is decided not in the superconductor, but in the normal conductor. The circular sections K and the annular ring R in the figure have the same potential because the electrostatic potential in a superconductor is constant. Potential theory applied to the interior of the normal conductor then tells us what part of I , takes the path through the inner cylinder.

This current enters the superconductor at K and must finally reach the lower lead. As it cannot penetrate deeply into the superconductor, it can only go along the boundary of the superconductor, as sketched in the figure. It flows, in fact, across the plane R and there joins the current $I - I'$ that enters the outer surface of the superconductor from above. The full current then flows down the outer surface to the lower leads.

The uniqueness of the solution sketched here is again guaranteed by the theorem of Chap. 7 (a). To begin with, owing to the symmetry of the arrangement, the magnetic field is known for all bounda-

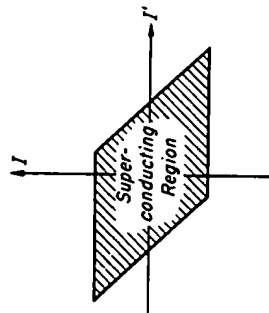


Fig. 9-2. Diagrammatic representation of Silsbee's hypothesis for a hollow superconducting cylinder. I is the net current in the superconducting cylinder; I' is the current in the coaxial wire.

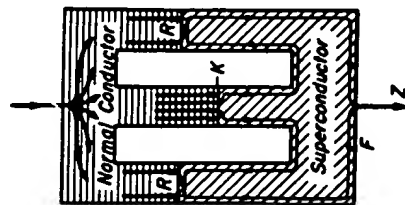


Fig. 9-3. Current distribution at the boundaries between normal and superconducting parts of a cylinder.

ries, e. g., the lower surface F of the superconductor. After solving the potential problem for the normal conductor (which is possible only in one way) our knowledge of I , allows us to find the field distribution first in the hollow space between the inner cylinder and the outer shell, secondly at the boundaries K and R of the superconductor, and therefore at all surfaces of the latter.

(c) Figure 9-4 represents a similar arrangement only in this case the whole shaded area is to be superconducting. Again we imagine the current I to be fed in at Z and carried back by a third cylinder C_3 coaxial with C_1 and C_2 . This shields the field from outside because a curve enclosing it encloses a net current zero. The circuit for the current I_1 flowing in C_1 is completed by the inner walls of C_2 and the two superconducting caps. It does not affect the outside at all, so long as the superconducting parts are thick compared with the penetration depth, but neither can it be influenced from the outside. It is a persistent current in what is here actually a doubly connected body. Its energy is substantially of magnetic nature and is located in the hollow space between C_1 and C_2 and has the form $a I_1^2$; the value of the constant a is of no importance.

One can also consider this apparatus from another point of view. The parts formed by sections at A and B can be regarded as superconductors in parallel in the sense of Chap. 2. In order to permit the current strength I_2 in the cylinder C_2 a current $I_1 + I_2$ must flow along its outer walls because the inner wall carries the current $-I_1$. Consequently the energy located between C_2 and C_3 (and to an unimportant degree also in the protecting layer of C_2) is of the form $\gamma (I_1 + I_2)^2$. Writing the total energy $a I_1^2 + \gamma (I_1 + I_2)^2$ in the form $\frac{1}{2} (\phi_{11} I_1^2 + \phi_{22} I_2^2 + 2 \phi_{12} I_1 I_2)$ we have $\phi_{12} = \gamma$. According to eq. 2-6 it follows that if there were no current in the system initially, I_1 would remain zero after switching on the current I , while any initial current I_1 would remain unchanged by switching on I .

These considerations, although leading to no new results, nevertheless show the intimate relations between the discussion of Chap. 2 and the theory explained in Chap. 3 and later chapters.

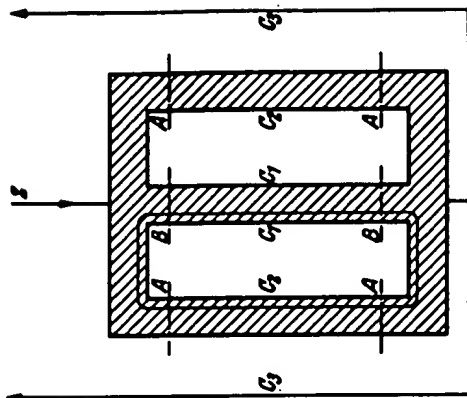


Fig. 9-4. Doubly connected superconductor in the same arrangement as in Fig. 9-3.

The requirements that \mathbf{H}_t goes over continuously into H_t at $r = R_c$ and to H_i at $r = R_i$ serve to determine the constants C and D .

If the walls of the cylinder are thick compared with β^{-1} we can in eq. 10-4 neglect the first term when $r = R_i$ and the second term when $r = R_c$, as we did in Chap. 9 (a). We then have to put

$$C = \frac{H_c}{I_0(\iota\beta R_c)}, \quad D = \frac{H_i}{\iota H_0(\iota\beta R_i)} \quad (10-6)$$

This leads back to eq. 10-1 for the layer at the outer boundary, while for the neighborhood of the inner boundary it follows that

$$\mathbf{H}_t = H_i \frac{H_0(\iota\beta r)}{H_0(\iota\beta R_i)}, \quad i_\theta = -H_i \frac{H_1(\iota\beta r)}{\iota \sqrt{\lambda} H_0(\iota\beta R_i)} \quad (10-7)$$

Since $H_1(\iota\beta r)$ is negative while $\iota H_0(\iota\beta R)$ is positive, the current for positive H_i has again the direction of increasing θ . A field-free region is located between the two protective layers where these equations hold.

Let us choose $H_c = 0$. If we ascribe to the cylinder a finite length which, however, is great compared with its diameter, eqs. 10-7 are still valid except in the neighborhood of the ends. Here we have an example of a persistent current, because indeed a hollow cylinder is a doubly connected body.

Let us assume the cylinder to be thin ($R_c - R_i \ll \beta^{-1}$) and choose $H_c = H_i$. Writing R_m for the arithmetic mean between R_c and R_i , the first terms of the expansion will now suffice:

$$\mathbf{H}_t = (\mathbf{H}_t)_{R_m} + \left(\frac{\partial \mathbf{H}_t}{\partial r} \right)_{R_m} (r - R_m)$$

If the right-hand side has to assume the same value, H_c at $r = R_i$, i. e., at $r - R_m = -\frac{1}{2}(R_c - R_i)$, as it does at $r = R_c$, i. e., at $r - R_m = \frac{1}{2}(R_c - R_i)$, then $(\partial \mathbf{H}/\partial r)_{R_m}$ must be zero; consequently according to eq. 10-5 (i_θ) $_{R_m}$ is also zero. This again confirms the general argument of Chap. 7 (b) for thin specimens.

The solutions given in eqs. 10-1 and 10-2, 10-4 and 10-5 remain valid for noncubic crystals provided the ellipsoid of the tensor $\lambda_{\alpha\beta}$ has an axis of symmetry (say x_3) in the direction of the axis of the cylinder, and the two principal values λ_1 and λ_2 coincide. Then for this problem the supermomentum is in fact always in the same direction as the supercurrent, just as in the cubic case, while

$$\beta_1 = \frac{1}{c \sqrt{\lambda_1}} \quad (10-8)$$

replaces β in the calculation.

(c) Now let us imagine a solid cylinder of radius R with no longitudinal current, placed in a field perpendicular to its axis — a transverse field. The field does not remain homogeneous as the lines of force must go around the cylinder if the latter is not too thin, i. e., they are deflected by it as shown in Fig. 1-5. If we are not satisfied with the approximation used in the figure, which regards the superconductor as completely impenetrable to the field (a case for which the distortion of the field can easily be

CHAPTER 10

The Cylinder in a Homogeneous Magnetic Field

(a) We now place a homogeneous superconducting cylinder in a longitudinal magnetic field; no current flows in the direction of its axis; the external field has everywhere the same strength $\mathbf{H}_t = H^0$ outside the surface of the cylinder.

In the interior of the cylinder \mathbf{H}_t has to satisfy the equation $\Delta u - \beta^2 u = 0$ and must moreover depend only on the distance r from the axis. Like the current density i , in Chap. 8 (b) which satisfied the same conditions, \mathbf{H}_t must therefore be proportional to $I_0(\iota\beta r)$. The boundary condition that \mathbf{H}_t be continuous is then obviously satisfied by

$$\mathbf{H}_t = H^0 \frac{I_0(\iota\beta r)}{I_0(\iota\beta R)} \quad (10-1)$$

We find the current density from $\mathbf{i} = c \operatorname{curl} \mathbf{H}$. According to eq. 8-1 this reads:

$$i_r = i_z = 0, \quad i_\theta = -c \frac{\partial \mathbf{H}_t}{\partial r} = \iota H^0 \frac{I_1(\iota\beta r)}{\sqrt{\lambda} I_0(\iota\beta R)} \quad (10-2)$$

[From eq. 8-7 $dI_0(x)/dx = -I_1(x)$]. From the form of these two Bessel functions, discussed in Chap. 8 (b) it also follows here that the influence of the field on a thick wire is confined to a protecting layer of thickness β^{-1} . The currents that provide this protection flow in the direction of increasing θ when H^0 is positive because $-I_1(\iota\beta r)$ is positive. This corresponds to the rule that current, field strength, and inner normal to the superconductor — here the negative r direction — form a right handed system. For a thin wire ($\beta R \ll 1$) the flat minimum of $I_0(\iota\beta r)$ at $r = 0$ shows that the field penetrates almost without loss. In this case

$$i_\theta = -\frac{1}{2} \frac{H^0 \beta r}{\sqrt{\lambda}} \quad (10-3)$$

This becomes identical with eq. 7-29 if one puts $L = R$ and $\tau_a = -r/2 R$. (b) Now let us consider a hollow cylinder with radii R_i and R_c having a field strength $\mathbf{H}_t = H_i$ in the bore, whereas outside there is a homogeneous field $\mathbf{H}_t = H_c$. Within the superconductor \mathbf{H}_t has to satisfy the same differential equation as in case (a); but for the reasons we have discussed in Chap. 9 (c) in connection with the hollow cylinder carrying a current, we now write down the analogous expression to eq. 9-3:

$$\mathbf{H}_t = C I_0(\iota\beta r) + \iota D H_0(\iota\beta r) \quad (10-4)$$

From this it follows, as in (a) (compare also eq. 9-5) that

$$i_\theta = -c \frac{\partial \mathbf{H}_t}{\partial r} = \iota c \beta C I_1(\iota\beta r) - c \beta D H_1(\iota\beta r) \quad (10-5)$$

calculated by potential theory) we have to try to determine the internal and the external field simultaneously. We come here for the first time to an example in which the external field cannot be specified in advance. The uniqueness theorem of Chap. 7 (a) is no longer applicable; instead we shall need a more general uniqueness theorem worked out in Chap. 12 (d).

Introduce rectangular coordinates in a plane perpendicular to the wire to supplement the polar coordinates r and θ used hitherto:

$$x = r \cos \theta, \quad y = r \sin \theta$$

Suppose the intensity of the homogeneous field has the positive direction and magnitude H^0 . Its potential would then be

$$\Phi = -H^0 x = -H^0 r \cos \theta$$

According to potential theory a completely impenetrable cylinder would act at points outside it as a dipole sheet, and its potential would be of the form¹ $(a/r) \cos \theta$, with $a = R^2$. We therefore seek a rigorous solution of the problem in the following form with a at first undetermined:

$$\Phi = -H^0 \left(r + \frac{a}{r} \right) \cos \theta \quad (10-9)$$

Because $\mathbf{H} = -\text{grad } \Phi$ it follows that

$$\begin{aligned} \mathbf{H}_r &= -\frac{\partial \Phi}{\partial r} = H^0 \left(1 - \frac{a}{r^2} \right) \cos \theta \\ \mathbf{H}_\theta &= -\frac{1}{r} \frac{\partial \Phi}{\partial \theta} = -H^0 \left(1 + \frac{a}{r^2} \right) \sin \theta \end{aligned} \quad (10-10)$$

(We see that eq. 10-10 yields $\mathbf{H}_r = 0$ for $a = R^2$ and $r = R$, corresponding to the case of impenetrability.)

\mathbf{H}_θ is therefore proportional to $\sin \theta$ on the boundary as well as in the external space. Remembering the intimate connection between the current density and the tangential component of magnetic field, which we first noted when discussing thick specimens, it is natural to put inside the cylinder

$$\mathbf{i}_x = \mathbf{i}_y = 0, \quad \mathbf{i}_z = f(r) \sin \theta \quad (10-11)$$

Since \mathbf{i}_z must be a solution of $\Delta u - \beta^2 u = 0$, the differential eq. 8-4 with $k = 0$ and $n = 1$ must be satisfied by $f(r)$. Furthermore $f(r)$ must remain finite and continuous at $r = 0$ so that

$$f(r) = C I_1(\iota \beta r), \quad \mathbf{i}_z = C I_1(\iota \beta r) \sin \theta \quad (10-12)$$

where C is an integration constant. From $\mathbf{H} = -c \lambda \text{curl } \mathbf{i}$ and eq. 8-1 it follows therefore that

$$\begin{aligned} \mathbf{H}_r &= -\frac{c \lambda}{r} \frac{\partial \mathbf{i}_z}{\partial \theta} = -\frac{c \lambda C}{r} \iota I_1(\iota \beta r) \cos \theta \\ &= -\frac{\sqrt{\lambda} C}{\beta r} \iota I_1(\iota \beta r) \cos \theta \end{aligned} \quad (10-13)$$

¹ $\iota r^{-1} \cos \theta$ is the real part of the function ζ^{-1} of the complex variable $\zeta = x + \iota y$ and in this way a solution of the potential equation.

and, noting one of the eqs. 8-7,

$$\mathbf{H}_\theta = c \lambda \frac{\partial \mathbf{i}_z}{\partial r} = -\sqrt{\lambda} C [I_0(\iota \beta r) - \frac{1}{\iota \beta r} I_1(\iota \beta r)] \sin \theta \quad (10-14)$$

For boundary conditions we have the continuity of the two components of \mathbf{H} at $r = R$. These can be satisfied by the above expressions, and this justifies our chosen procedure. As a comparison of eqs. 10-13 and 10-14 with 10-10 shows, we have only to adjust the constants a and C so that

$$H^0 \left(1 - \frac{a}{R^2} \right) = \frac{\sqrt{\lambda} C}{\iota \beta R} I_1(\iota \beta R) \quad (10-15)$$

$$H^0 \left(1 + \frac{a}{R^2} \right) = \sqrt{\lambda} C \left[I_0(\iota \beta R) - \frac{1}{\iota \beta R} I_1(\iota \beta R) \right]$$

These requirements yield:

$$\begin{aligned} C &= \frac{2 H^0}{\sqrt{\lambda} I_0(\iota \beta R)}, \quad 1 - \frac{a}{R^2} = \frac{2}{\iota \beta R} \frac{I_1(\iota \beta R)}{I_0(\iota \beta R)} \\ \mathbf{i}_z &= \frac{2 H^0 \sin \theta \iota I_1(\iota \beta r)}{\sqrt{\lambda} I_0(\iota \beta R)} \end{aligned} \quad (10-16)$$

According to eqs. 10-13 and 10-14 the magnetic lines of force in the interior of the cylinder must be such that \mathbf{i}_z is constant. For thick cylinders this means

$$\frac{\iota I_1(\iota \beta r)}{I_0(\iota \beta R)} = -e^{-\beta(R-r)} \quad (10-17)$$

The right-hand side of the equation for a becomes zero, and a assumes the potential theory value R^2 , and at the surface, according to eq. 10-10 we shall have

$$(\mathbf{H}_\theta)_R = -2 H^0 \sin \theta$$

The maximum $2 H^0$ of $|\mathbf{H}_\theta|$ illustrates the doubling of the field strength due to field deformation discussed in Chap. 1 (g). From eqs. 10-16 and 10-17, however, it follows that

$$\mathbf{i}_z = -2 H^0 \lambda^{-\frac{1}{2}} e^{-\beta(R-r)} \sin \theta = \lambda^{-\frac{1}{2}} (\mathbf{H}_\theta)_R e^{-\beta(R-r)}$$

The same result would be obtained from eq. 7-10 by adapting to a cylindrical surface the equation given there for a plane boundary. Such a step would be justified for a thick cylinder. The protecting layer obeys the same laws here as at a plane surface. \mathbf{i}_z is negative for positive θ , i. e., in the upper part of Fig. 1-5, so the current is flowing away from the reader; this fact corresponds to the general rule that current, magnetic field, and internal normal form a right-handed system.

According to eq. 10-17 and the equation for a in 10-16 we have, for a thick cylinder

$$a = R^2 \left(1 - \frac{2}{\beta R} \right)$$

The magnetic moment is decreased by the factor $(1 - 2/\beta R)$ compared with the case of a completely vanishing penetration depth ($\beta \rightarrow \infty$). For thin cylinders ($\beta R \ll 1$), $I_0(\iota \beta R) = 1$ and $I_1(\iota \beta R) = \frac{1}{2} \iota \beta R$. (Compare the series 8-6). The right-hand side of equation 10-16 for a now becomes equal to unity and $a = 0$. According to eq. 10-9 the field now penetrates the cylinder without being deflected and no longer induces any current in it, because, according to eq. 10-16 i , vanishes like βR in agreement with eq. 7-29.

According to eq. 8-6 we have the following series expansions:

$$\begin{aligned} \frac{I_1(\iota x)}{\frac{1}{2} \iota x} &= 1 + \frac{(\frac{1}{2} x)^2}{1 \cdot 2!} + \frac{(\frac{1}{2} x)^4}{2! \cdot 3!} + \dots + \frac{(\frac{1}{2} x)^{2m}}{m! (m+1)!} + \dots \\ I_0(\iota x) &= 1 + \frac{(\frac{1}{2} x)^2}{(1!)^2} + \frac{(\frac{1}{2} x)^4}{(2!)^2} + \dots + \frac{(\frac{1}{2} x)^{2m}}{(m!)^2} + \dots \end{aligned}$$

In the second series the coefficients of all powers of x are greater than the corresponding coefficients in the first series, therefore $I_0(\iota x) > 2I_1(\iota x)/\iota x$, and it increases with increasing x more rapidly than $2I_1(\iota x)/\iota x$. The right-hand side of eq. 10-16 for a is therefore smaller than unity for all values of βR and continually decreases with increasing R but without becoming negative. Therefore a increases with increasing R monotonically from 0 to R^2 , the limit already mentioned.

Figure 10-1 shows the form of the lines of force for three different values of βR . In the external space the lines follow the same course as with a diamagnetic specimen. However, whereas inside a diamagnetic body they would be straight, here they are more or less curved.

If the temperature is lowered, starting from the transition temperature, the penetration depth $\beta^{-1} = c/\sqrt{\lambda}$ is at first great, and so βR is a small number for any given value of R . Later β^{-1} decreases and βR increases. The figures represent in this way the gradual expulsion of the field from the interior of the specimen. The final phase, $\beta R \gg 1$ is shown in Fig. 1-5.

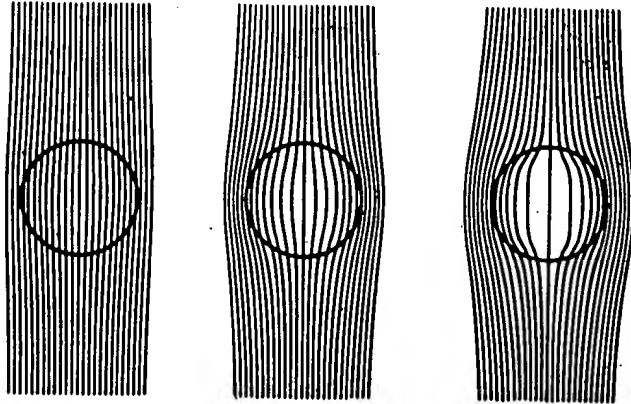


Fig. 10-1. Lines of force for a thin superconducting cylinder in a transverse homogeneous magnetic field for different ratios of diameter to penetration depth. a) $\beta R = 1$; b) $\beta R = 2$; c) $\beta R = 3$

As the current here has only one component i_z , the solution implied by eqs. 10-12, 10-13, and 10-14 can be taken over for noncubic crystals under the same conditions as set up in Chap. 8 (e).

(d) No rigorous solution can yet be given for an elliptical cylinder in an external field; just as was the case for the cylinder carrying a current treated in Chap. 8 (d), we must confine ourselves again to the approximation that holds only for "thick" cylinders. The boundary curve must then be a field line. The solution is trivial for the longitudinal field: everywhere in the external space the field strength H_z is constant and equal to H_0 , and the current density can be calculated by eq. 7-10.

For the transverse field, however, we assume that the field strength forms an angle $\theta_0 < \frac{1}{2}\pi$ with the a axis at a great distance from the cylinder. For the description of the field we use, as in Chap. 8 (e) a function of the complex variable $\zeta = x + \iota y$, which we shall call $W = U + \iota V$, and take U as the potential. We define W in terms of the complex parameter $\chi = \psi + \iota \varphi$, namely,

$$W = -\frac{1}{2} H_0 \sqrt{a^2 - b^2} \left(e^{\chi - \iota \theta_0} + \frac{a+b}{a-b} e^{-\chi + \iota \theta_0} \right) \quad (10-18)$$

$$\zeta = \sqrt{a^2 - b^2} \cosh \chi$$

The second of these equations follows from eq. 8-26 by putting $a = 1$ there. In analogy to eq. 8-27 we have here

$$x = \sqrt{a^2 - b^2} \cosh \psi \cos \varphi, \quad y = \sqrt{a^2 - b^2} \sinh \psi \sin \varphi \quad (10-19)$$

and the curves $\psi = \text{constant}$ are the confocal ellipses

$$\frac{x^2}{\cosh^2 \psi} + \frac{y^2}{\sinh^2 \psi} = a^2 - b^2 \quad (10-20)$$

Let the contour of the cylinder correspond to the value ψ_0 , so that

$$\sqrt{a^2 - b^2} \cosh \psi_0 = a, \quad \sqrt{a^2 - b^2} \sinh \psi_0 = b$$

$$e^{\pm \psi_0} = \sqrt{\frac{a+b}{a-b}} \quad (10-21)$$

The curves $\varphi = \text{constant}$, however, are the hyperbolas confocal to these ellipses:

$$\frac{x^2}{\cos^2 \varphi} - \frac{y^2}{\sin^2 \varphi} = a^2 - b^2 \quad (10-22)$$

ψ and φ are called elliptical coordinates. To make them single valued we restrict them to the ranges of values 0 to $+\infty$ for ψ and 0 to 2π for φ . Each of the above hyperbolas then corresponds to four φ values: if $\varphi = \varphi_0$ is the semi-axis in the first quadrant ($x > 0, y > 0$), then $\varphi = \pi - \varphi_0$ is the semi-axis in the second quadrant ($x < 0, y > 0$), $\varphi = \pi + \varphi_0$ that in the third quadrant ($x < 0, y < 0$) and $\varphi = 2\pi - \varphi_0$ in the fourth ($x > 0, y < 0$).

*The assumption that $\theta_0 > \frac{1}{2}\pi$ leads to nothing new.

From eq. 10-18 it follows that

$$\begin{aligned} U &= -\frac{1}{2} \frac{H^0}{a^2} \sqrt{a^2 - b^2} \left\{ e^{\psi} + \frac{a+b}{a-b} e^{-\psi} \right\} \cos(\varphi - \theta_0) \\ V &= -\frac{1}{2} \frac{H^0}{a^2} \sqrt{a^2 - b^2} \left\{ e^{\psi} - \frac{a+b}{a-b} e^{-\psi} \right\} \sin(\varphi - \theta_0) \end{aligned} \quad (10-23)$$

Because of the way they were derived from eq. 10-18, U and V are solutions of the potential equation. ψ is infinite at infinity, according to eq. 10-19. Therefore at infinity

$$U = -\frac{1}{2} \frac{H^0}{a^2} \sqrt{a^2 - b^2} e^{\psi} (\cos \varphi \cos \theta_0 + \sin \varphi \sin \theta_0) = -H^0 (x \cos \theta_0 + y \sin \theta_0)$$

The field is therefore homogeneous at infinity, and inclined at an angle θ_0 to the x axis. The field line $V = 0$ consists first of those parts of the hyperbolas $\varphi = \theta_0$ and $\varphi = \pi + \theta_0$ which lie outside the ellipse ψ_0 (since these formulas are valid outside), and secondly of the ellipse ψ_0 ; because according to eq. 10-21 on this ellipse

$$e^{\psi_0} = \frac{a+b}{a-b} e^{-\psi_0}$$

The expression 10-18 thus satisfies all the imposed conditions.

We proceed to the calculation of $|\mathbf{H}| = |d\mathbf{W}/d\zeta|$. From eq. 10-18

$$\begin{aligned} \frac{d\mathbf{W}}{d\zeta} &= \frac{(d\mathbf{W}/d\chi)}{(d\zeta/d\chi)} = -\frac{H^0}{2 \sinh \chi} \left(e^{x-i\theta_0} - \frac{a+b}{a-b} e^{-x+i\theta_0} \right) \\ &= \frac{H^0 \left[\frac{a+b}{a-b} e^{-\psi-i(\varphi-\theta_0)} - e^{\psi+i(\varphi-\theta_0)} \right]}{2 (\sinh \psi \cos \varphi + i \cosh \psi \sin \varphi)} \end{aligned}$$

Along the ellipse ψ_0 we have from eq. 10-21

$$|\mathbf{H}| = \left| \frac{d\mathbf{W}}{d\zeta} \right| = \frac{H^0 (a+b)}{\sqrt{a^2 \sin^2 \varphi + b^2 \cos^2 \varphi}}$$

The maximum of this expression is at the point where

$$\tan \varphi = -\frac{b^2}{a^2} \cot \theta_0, \quad \text{i. e., } \frac{y}{x} = -\frac{b^3}{a^3} \cot \theta_0$$

If a diameter of the ellipse is drawn in the direction θ_0 , the conjugate diameter (parallel to the tangents at the ends of the first one) is given by

$$\frac{y}{x} = -\frac{b^2}{a^2} \cot \theta_0$$

If $b \ll a$ the maximum field therefore lies considerably nearer to the major axis of the ellipse than this diameter, except when $\theta_0 = 0$ or $\frac{1}{2}\pi$. The maximum value itself amounts to

$$|\mathbf{H}|_{\max} = H^0 \left(\frac{1}{a} + \frac{1}{b} \right) \sqrt{\frac{1}{a^2 \sin^2 \theta_0} + b^2 \cos^2 \theta_0} \quad (10-24)$$

For $\theta_0 = 0$ the factor multiplying H^0 becomes $(1 + b/a)$ and is thus smaller than the factor 2 appearing in the circular cylinder. For $\theta = \frac{1}{2}\pi$ however, the factor becomes $1 + a/b > 2$. This confirms the statement made in Chap. 1 (g) about the intensifying of the field. It is at once evident that this intensification is greater when the cylinder forces the field to diverge around its major axis than if it exposed only its minor axis to the field.

The expression 10-24 is needed to calculate the limiting value of H^0 that destroys the superconductivity in the cylinder [Chap. 17 (f)].

CHAPTER 11

The Sphere in a Homogeneous Magnetic Field

(a) We introduce polar coordinates in space, r, θ, φ , forming a right-handed system in that order (Fig. 11-1). The following equations hold for the curl of a vector \mathbf{A}

$$\begin{aligned} \text{curl } \mathbf{A} &= \frac{1}{r \sin \theta} \left[\frac{\partial}{\partial \theta} (\sin \theta \mathbf{A}_\varphi) - \frac{\partial \mathbf{A}_\theta}{\partial \varphi} \right] \\ \text{curl}_\theta \mathbf{A} &= \frac{1}{r \sin \theta} \frac{\partial \mathbf{A}_r}{\partial \varphi} - \frac{1}{r} \frac{\partial(r \mathbf{A}_\varphi)}{\partial r} \\ \text{curl}_\varphi \mathbf{A} &= \frac{1}{r} \frac{\partial(r \mathbf{A}_\theta)}{\partial r} - \frac{1}{r} \frac{\partial \mathbf{A}_r}{\partial \theta} \end{aligned} \quad (11-1)$$

The differential equation $\Delta u - \beta^2 u = 0$ in these coordinates reads:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \varphi^2} - \beta^2 u = 0 \quad (11-2)$$

We can solve this equation for the present problem by separation of the variables:

$$u = f(r) \sin \theta e^{i\varphi} \quad (11-3)$$

Direct calculation shows that

$$\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \varphi^2} = -\frac{2}{r^2} f(r) \sin \theta e^{i\varphi}$$

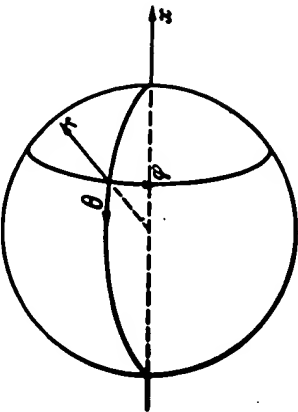
so we can divide eq. 11-2 by the factor $\sin \theta e^{i\varphi}$ common to all terms and we are left with the ordinary differential equation for $f(r)$:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{df}{dr} \right) - \left(\beta^2 + \frac{2}{r^2} \right) f = 0 \quad (11-4)$$

The solution of this that remains finite at $r = 0$ is

$$f(r) = \frac{1}{\beta r} \cosh(\beta r) - \left(\frac{1}{\beta r}\right)^2 \sinh(\beta r) \\ = \frac{(\beta r)}{3} + \frac{(\beta r)^3}{5 \cdot 3!} + \dots + \frac{(\beta r)^m}{(m+2)m!} + \dots \quad (11-5)$$

f is positive because $\tanh \beta r < \beta r$ for all positive values of r . For large values of βr



$$f = \frac{1}{2} (\beta r)^{-1} e^{\beta r} \quad (11-6)$$

(b) Let the polar axis $\theta = 0$ and likewise the positive x axis be in the direction of the homogeneous magnetic field. If the field were undisturbed its potential would be

$$\Phi = -H^0 r \cos \theta$$

Fig. 11-1. The polar coordinates r, θ, φ . The r arrow is pointed upwards.

If the sphere were completely impenetrable to the lines of force it would act as a dipole, as shown by potential theory and as will be confirmed later. This would contribute to the potential a term of the form¹ $r^{-2} \cos \theta$. Therefore in analogy to the procedure of Chap. 10 (c) we now seek a solution for the space outside the sphere in the form

$$\Phi = -H^0 \left(r + \frac{a}{r^2} \right) \cos \theta \quad (11-7)$$

Here $4\pi a H^0$ represents the magnetic moment of the sphere². With positive a it is in the negative x direction and thus opposite to the field. The magnetic field strength $H = -\text{grad } \Phi$ follows immediately from eq. 11-7:

$$H_r = -\frac{\partial \Phi}{\partial r} = H^0 \left(1 - \frac{2a}{r^3} \right) \cos \theta \\ H_\theta = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta} = -H^0 \left(1 + \frac{a}{r^3} \right) \sin \theta \\ H_\varphi = 0 \quad (11-8)$$

As can be expected from symmetry the lines of force lie in meridian planes $\varphi = \text{constant}$. According to Chap. 7 (c) the current must be perpendicular to the lines of force, at least for thick superconductors, and

¹ Together with r^{-1} itself, all its derivatives with respect to the rectangular coordinates x, y, z are also solutions of $\Delta u = 0$. But $\partial(r^{-1})/\partial x = -x/r^3 = -\cos \theta/r^2$ since we have chosen $x = r \cos \theta$.

² This is in Lorentz units. In electrostatic units the moment is $a H^0$.

near the surface, so we must expect it to flow along the latitude — circles $r = \text{const}$, $\theta = \text{constant}$. Therefore for the interior of the sphere we try

$$i_r = i_\theta = 0, \quad i_\varphi = C f(r) \sin \theta \quad (11-9)$$

If for $f(r)$ we assume the same function as in eq. 11-5, then according to (a) the components of the current

$$i_r = -i_\varphi \sin \varphi, \quad i_\theta = i_\varphi \cos \varphi$$

satisfy the differential equation $\Delta u - \beta^2 u = 0$. From the relation $H = -c \lambda \text{curl } i$ we have from eq. 11-1:

$$H_r = -\frac{c \lambda}{r \sin \theta} \frac{\partial(\sin \theta i_\varphi)}{\partial \theta} = -\frac{2\sqrt{\lambda}}{\beta r} C f(r) \cos \theta \\ H_\theta = -\frac{c \lambda}{r} \frac{\partial(r i_\varphi)}{\partial r} = \frac{\sqrt{\lambda} C}{\beta r} [\sinh(\beta r) - f(r)] \sin \theta \quad (11-10)$$

To check whether these equations are correct we show, as in Chap. 10 (c) that they fulfil the boundary conditions at the surface of the sphere $r = R$. These require the continuity of the two nonvanishing components of H . According to eqs. 11-8 and 11-10 we should have

$$H^0 \left(1 - \frac{2a}{R^3} \right) = -\frac{2\sqrt{\lambda}}{\beta R} C f(R) \\ H^0 \left(1 + \frac{a}{R^3} \right) = \frac{\sqrt{\lambda} C}{\beta R} [f(R) - \sinh(\beta R)]$$

As a matter of fact we can satisfy these conditions by means of the adjustable constants a and C . For this purpose we have to put

$$C = -\frac{3 H^0 \beta R}{2 \sqrt{\lambda} \sinh(\beta R)}, \quad a = \frac{1}{2} \left[1 - \frac{3 f(R)}{\sinh \beta R} \right] R^3 \quad (11-11)$$

Evidently i_φ is negative; the current flows against the arrow in Fig. 11-1. From eq. 11-10 we now have the equations

$$\frac{\partial}{\partial r} (r \sin \theta i_\varphi) dr + \frac{\partial}{\partial \theta} (r \sin \theta i_\varphi) d\theta = 0, \quad \text{i. e., } r \sin \theta i_\varphi = \text{constant}$$

or $r f(r) \sin^2 \theta = \text{constant}$. These, with $\varphi = \text{constant}$, determine the magnetic lines of force in the interior.

(c) The discussion proceeds in the same way as in Chap. 10 (c). From eqs. 11-9, 11-10, and 11-11 it follows that for a large sphere ($\beta R \gg 1$) and high values of βr that

$$i_\varphi = -\frac{3 H^0 R}{2 \sqrt{\lambda}} e^{-\beta(R-r)} \sin \theta \\ H_r = 0, \quad H_\theta = -\frac{3 H^0 R}{2 r} e^{-\beta(R-r)} \sin \theta \quad (11-12)$$

Again this means the formation of a protective layer around a field-free interior. Furthermore, we conclude from eqs. 11-11 and 11-6 that

$$a = \frac{1}{2} \left(1 - \frac{3}{\beta R} \right) R^3 \quad (11-13)$$

Using this value it follows from eq. 11-8 in agreement with eq. 11-12 that at $r = R$:

$$\mathbf{H}_r = 0, \quad \mathbf{H}_\theta = -\frac{3}{2} H^0 \sin \theta \quad (11-14)$$

The first equation proves that in this approximation the sphere appears from the outside as if it were totally impenetrable to the lines of force; the second equation proves that the intensification of the field due to its distortion leads to a maximum one and a half times the original field strength H^0 , as already mentioned in Chap. 1 (g). Figure 1-5 is valid qualitatively also for the field distribution in a meridian plane of the sphere in spite of the fact that it is drawn for the cylindrical problem. For small βR values, however, according to eq. 11-5 $I(R)$ becomes $(1/3)\beta R$, so from eq. 11-11 we have

$$a = 0 \quad (11-15)$$

As at the same time $C = -\frac{3H^0}{2\sqrt{\lambda}}$, it follows from eq. 11-9 that

$$i_\varphi = -\frac{1}{2} H^0 \left(\frac{\beta r}{\sqrt{\lambda}} \right) \sin \theta \quad (11-16)$$

and, from eq. 11-10 that

$$\mathbf{H}_r = H^0 \cos \theta, \quad \mathbf{H}_\theta = -H^0 \sin \theta \quad (11-17)$$

According to the last equation \mathbf{H} is in the x direction and has the magnitude H^0 . The magnetic field penetrates the sphere without hindrance as was to be expected from Chap. 7 (f)³, whereas eq. 11-16 for i_φ has the same general form as eq. 7-29. Choosing the length of the superconductor L equal to R in order to duplicate eq. 11-16 one has to put $-\frac{1}{2}(\tau/R) \sin \theta$ for the pure number τ_a which depends only on the position of the origin in the superconductor.

We conclude from the expansion 11-5 and the known series

$$\sinh(\beta R) = \beta R + \frac{(\beta R)^3}{3!} + \frac{(\beta R)^5}{5!} + \dots + \frac{(\beta R)^{2m+1}}{(2m+1)!}$$

that $\sinh(\beta R)$ increases faster with increasing βR than $I(R)$. Therefore by eq. 11-11 a grows monotonically with βR from 0 to $\frac{1}{2}R^3$, the magnetic

³ It follows from eq. 11-10 for the center of the sphere $r = 0$ exactly

$$(\mathbf{H}_r)_{r=0} = \frac{H^0 \beta R \cos \theta}{\sinh(\beta R)}, \quad (\mathbf{H}_\theta)_{r=0} = -\frac{H^0 \beta R \sin \theta}{\sinh(\beta R)}$$

This gives \mathbf{H} the direction of the x axis, as was to be expected from symmetry, and the magnitude $H^0 \beta R / \sinh(\beta R)$. This can be used to confirm the mean value theorem of eq. 7-25.

moment $4\pi a H^0$ goes from 0 to $2\pi R^3 H^0$, and the moment per unit volume and unit field strength increases from 0 to $\frac{3}{2}$.

A nonmagnetic layer, e. g., of colloidal spheres of mercury dispersed in gelatine, must become increasingly diamagnetic below the transition temperature, 4.17° K, the greater the moment per unit volume due to the spheres. If there are N such spheres per unit volume, the latter has a moment $4\pi a N H^0$; the permeability is therefore $\chi = 4\pi a N$. If each sphere has a radius R and they occupy a fraction V per unit volume, then $N = 3V/4\pi R^3$ so that

$$\chi = \frac{3V a}{\pi R^3}$$

For large values of βR :

$a = \frac{1}{2} R^3$ according to Fig. 11-2. Relative susceptibility of a slab containing superconducting colloidal mercury spheres as a function of temperature. (After Shoenberg.)

$$\chi_\infty = \frac{3V}{2\pi}$$

and in this way we get for $\beta R \ll 1$ a somewhat better approximation than used above:

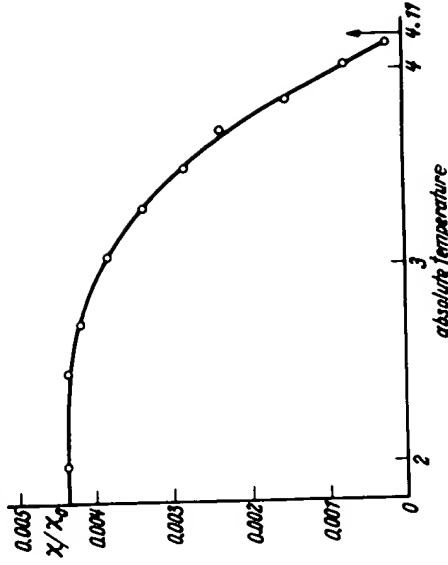
$$\frac{\chi}{\chi_\infty} = \frac{a}{\frac{1}{2} R^3} = 1 - \frac{3}{\sinh(\beta R)} = \frac{1}{15} (\beta R)^2 \quad (11-18)$$

(d) Shoenberg⁴ [Chap. 1 (c)] used the above method to determine the superconductivity constant λ as a function of temperature. He knew from the amount of mercury in emulsion what the permeability χ_0 would be if the βR of the small spheres were great compared with unity. Actually the permeability was only some thousandths of this (see Fig. 11-2) and dropped much lower still as the transition temperature was approached. Shoenberg knew only that the average radius of the spheres was about 0.5×10^{-5} cm. To obtain information about β he started from eq. 11-18. If we indicate values of χ , β , and λ at $T = 2.5^\circ \text{K}$ by an inferior 2.5, we have, from eqs. 11-18 and 6-7

$$\frac{\chi}{\chi_{2.5}} = \left(\frac{\beta}{\beta_{2.5}} \right)^2 = \frac{\lambda_{2.5}}{\lambda}$$

⁴D. Shoenberg, *Nature*, 143, 434 (1939).

E. Laurmann and D. Shoenberg, *Nature*, 160, 747 (1948).



By means of this equation Shoenberg was able to plot his experimental data as in Fig. 11-3, which shows $|\lambda/\lambda_{2.5}|$ as a function of T . They agree excellently with the values found by Appleyard and co-workers⁵ [Chap. I (c)] using another method [see Chap. 18 (e)]. λ becomes infinite at T , like $(T, -T)^{-1}$ because χ goes to zero like $(T, -T)$ in Fig. 11-2.

(e) If we specify a line of force by its distance in the undistorted part of the field from the central line of force that is directed toward the center of the sphere, its equation can easily be derived from eq. 11-7 and reads

$$\left(r^2 - \frac{2a}{r}\right) \sin^2 \theta = C^2, \quad \varphi = \text{constant}$$

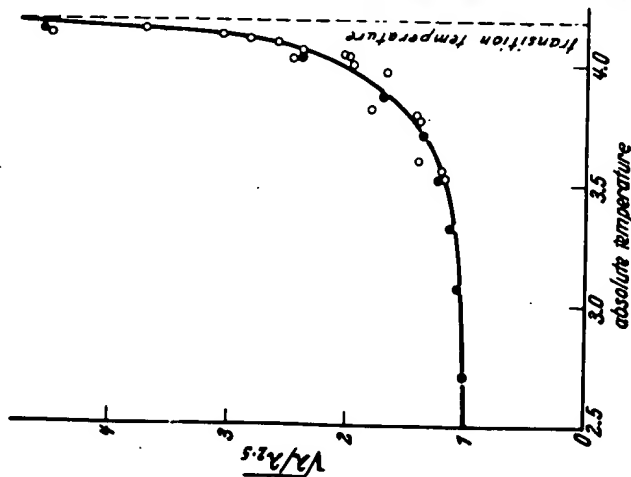


Fig. 11-3. The superconductivity constant λ for mercury as a function of temperature. ● measurements of Appleyard, Bristow, and H. London; ○ measurements of Shoenberg.

(f) The eqs. 11-9, 11-10, and 11-11 remain true for noncubic crystals if the ellipsoid of the tensor $\lambda_{\alpha\beta}$ has rotational symmetry and the axis of symmetry lies in the x direction. Only then β can be replaced by $\beta_1 = 1/c \sqrt{A_1}$ where A_1 is the principal value of the tensor for a direction perpendicular to the axis of symmetry.

⁵T. S. Appleyard, T. R. Bristow, and H. London, *Nature*, 148, 433 (1939).

CHAPTER 12

Persistent Currents

(a) A classical method for the treatment of electromagnetic problems uses the vector potential \mathbf{A} in conjunction with the scalar potential Φ . In the static case Φ becomes the electrostatic potential and it is therefore a generalization of the latter. \mathbf{A} and Φ are defined by requiring

$$\mathbf{B} = \text{curl } \mathbf{A} \quad (12-1)$$

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \text{grad } \Phi \quad (12-2)$$

From these it follows at once that

$$\text{div } \mathbf{B} = 0, \quad \frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \frac{1}{c} \text{curl } \frac{\partial \mathbf{A}}{\partial t} = -\text{curl } \mathbf{E}$$

which agrees with the fundamental eqs. I and III (Chap. 3). To obtain the fundamental eqs. II and IV also, we must now add a condition on $\text{div } \mathbf{A}$, which we may do because no vector is completely defined by giving only its curl. We require that

$$\text{div } \mathbf{A} + \frac{\varepsilon \mu}{c^2} \frac{\partial \Phi}{\partial t} = 0 \quad (12-3)$$

According to eqs. 12-2 and 3-1 we now have

$$\begin{aligned} \text{div } \mathbf{D} &= \text{div } (\varepsilon \mathbf{E}) = \varepsilon \text{div } \mathbf{E} + (\mathbf{E} \cdot \text{grad } \varepsilon) \\ &= -\frac{\varepsilon}{c} \frac{\partial}{\partial t} \text{div } \mathbf{A} - \varepsilon \Delta \Phi + (\mathbf{E} \cdot \text{grad } \varepsilon) \\ &= \frac{\varepsilon^2 \mu}{c^2} \frac{\partial^2 \Phi}{\partial t^2} - \varepsilon \Delta \Phi + (\mathbf{E} \cdot \text{grad } \varepsilon) \end{aligned}$$

and if we subject Φ to the condition

$$\Delta \Phi - \frac{\varepsilon \mu}{c^2} \frac{\partial^2 \Phi}{\partial t^2} = -\rho + \frac{1}{\varepsilon} (\mathbf{E} \cdot \text{grad } \varepsilon) \quad (12-4)$$

we recover eq. IV ($\text{div } \mathbf{D} = \rho$). In order to obtain eq. II we use eqs. 12-1 and 12-3 and the vector rule 6-1 to obtain

$$\begin{aligned} \text{curl } \mathbf{B} &= \text{curl curl } \mathbf{A} = \text{grad div } \mathbf{A} - \Delta \mathbf{A} = -\text{grad} \left(\frac{\varepsilon \mu}{c^2} \frac{\partial \Phi}{\partial t} \right) - \Delta \mathbf{A} \\ &= \frac{\varepsilon \mu}{c} \left[\frac{\partial \mathbf{E}}{\partial t} + \frac{1}{c} \frac{\partial^2 \mathbf{A}}{\partial t^2} \right] - \frac{1}{c} \frac{\partial \Phi}{\partial t} \text{grad } (\varepsilon \mu) - \Delta \mathbf{A} \end{aligned} \quad (12-5a)$$

Also according to eqs. 3-2 and II:

$$\begin{aligned} \text{curl } \mathbf{B} &= \text{curl } (\mu \mathbf{H}) + \text{curl } \mathbf{M} = \mu \text{curl } \mathbf{H} - [\mathbf{H} \times \text{grad } \mu] + \text{curl } \mathbf{M} \\ &= \frac{\mu}{c} \left(\frac{\varepsilon \partial \mathbf{E}}{\partial t} + \mathbf{i} \right) - [\mathbf{H} \times \text{grad } \mu] + \text{curl } \mathbf{M} \end{aligned} \quad (12-5b)$$

The necessary and sufficient condition for the validity of eq. 11 follows by subtracting the right-hand sides of 12-5a and 12-5b:

$$\Delta A - \frac{\epsilon\mu}{c^2} \frac{\partial^2 A}{\partial t^2} = -\frac{\mu}{c} \mathbf{i} - \text{curl } \mathbf{M} + \frac{1}{c} \frac{\partial \Phi}{\partial t} \text{grad}(\epsilon\mu) + [\mathbf{H} \times \text{grad } u] \quad (12-6)$$

We accept eqs. 12-4 and 12-6 as valid throughout all space. The \mathbf{i} here always means the sum of ohmic and supercurrents.

The most frequent application of eq. 12-1 consists in the transformation of the integral $\int_C \mathbf{B} \cdot d\sigma$ over a surface C into the line integral around the boundary by Stokes' theorem:

$$\int_C (\mathbf{B} \cdot d\sigma) = \int_C (\mathbf{A} \cdot ds) \quad (12-7)$$



Fig. 12-1.
Illustration for Stokes' theorem, eq. 12-7. The normal vector $d\sigma$ points toward the reader.

Figure 12-1 shows the relation between the direction of the normal vector $d\sigma$ and the sense ds in which the line integral traverses the boundary. The justification for using the same symbol C to specify both surface and loop is that all surfaces with the same loop as boundary have the same integral $\int_C (\mathbf{B} \cdot d\sigma)$ because of $\text{div } \mathbf{B} = 0$.

(b) We now have to explain the concept of the multiply connected region. In a simply connected or singly connected region of space two closed curves C and C' which lie completely within the region, but are otherwise quite arbitrary, can be transformed into each other by continuous deformation without either of them leaving the region. In particular C can be contracted to a point, because C' can be chosen to be an infinitesimal loop around this point. Such curves also exist in a doubly connected region; we call them curves of the first kind. Besides these there are curves of the second kind which can be transformed in the described manner into each other but not into curves of the first kind. It is impossible to reduce them to a point (Fig. 12-2a). We have to distinguish n sets of curves for an n -ply connected region¹.

All curves of the same kind can be transformed into each other in the described manner but not curves of one set into curves of another set. The possibility of reduction to a point is reserved for curves of the first kind. We assign once and for all the same arbitrary sense of traversal to all curves of the same kind. The line integrals over such curves are defined to follow this sense of traversal, which we shall call the sense of the curve or circuit.

¹Curves that can be reduced by continuous deformation to a curve C_1 together with a curve C_2 within a triply connected region do not constitute a new kind of curve.
- A similar statement holds for n -ply connected regions.

In a singly connected region of space every finite and continuous scalar function Ψ is unique if its gradient is uniquely defined, e. g., by physical quantities, because for any closed curve C in the region

$$\oint_C (ds \cdot \text{grad } \Psi) = \int_C (d\sigma \cdot \text{curl grad } \Psi)$$

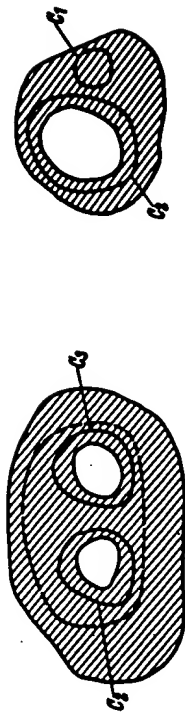


Fig. 12-2. (a) Curves C_1 and C_2 in a doubly connected region. (b) Curves C_1 and C_2 in a triply connected region. The dotted line is not a new kind of curve because it can be reduced to a curve C_2 together with a curve C_1 .

and the right side vanishes because $\text{curl grad } \Psi \equiv 0$. This conclusion holds only for curves of the first kind in a doubly connected region if Ψ is defined only within the region. Since these curves can be contracted to a point, we can draw surfaces of which they are the boundaries completely within the region of interest. For a curve of the second kind, such a surface necessarily extends outside the region. Otherwise it would also be possible to reduce these curves to a point. Consequently, for a curve of the second kind C_2 ,

$$\int_{C_2} (ds \cdot \text{grad } \Psi) = S_{C_2}$$

can differ from zero and be either positive or negative. However, the integral has the same value for all curves C_2 . For two such curves C_2 and C_2'

$$\int_{C_2} (ds \cdot \text{grad } \Psi) - \int_{C_2'} (ds \cdot \text{grad } \Psi) = \iint_C (d\sigma \cdot \text{curl grad } \Psi)$$

The surface integral extends over a surface bounded by the curves C_2 and C_2' lying completely within the region and is therefore zero because of the present theorem. In an n -ply connected region the integral

$\int_C (ds \cdot \text{grad } \Psi)$ has the same value for all curves C_m (any given $m \leq n$) but has different values for curves of different kind. It is zero for curves of the first kind, as before.

A doubly connected region is made simply connected by a cut Q , i. e., a surface intersecting every curve C_2 once and only once, destroying all C_2 as closed curves. All curves still remaining closed are now of the first kind. The boundaries of the cut necessarily lie in the surface of the region.

Otherwise Q would not cut all the curves C_2 . Except for this requirement there is complete freedom of choice of position and form of Q . ($n - 1$) cross-sectional cuts Q_m ($m = 2, 3, \dots, n$) are needed to produce a simply connected region from an n -ply connected one. Q_m cuts all closed curves C_m . In the single region formed in this way only closed curves of the first kind C_1 exist and the scalar Ψ is unique in such a region. Consider two points 1 and 2 lying on opposite sides of, and immediately adjacent to, the cut Q_m . Ψ differs at 1 and 2 by

$$\Psi_2 - \Psi_1 = \int_1^2 (ds \cdot \text{grad } \Psi) = \int_{C_m} (ds \cdot \text{grad } \Psi) = S_{C_m} \quad (12-7)$$

The points 1 and 2 must be chosen in such a way that the path from 1 to 2 that does not pass through the cut at Q_m has the same sense as the curve C_m . As S_{C_m} has the same value for all curves C_m the jump in Ψ at the cut is the same for all points on it.

These cuts are necessary if one wishes to apply Stokes' theorem in a multiply connected region to a vector ΨS , the product of a unique vector S with Ψ . Applied to the cut region

$$\int \text{div} (\Psi S) d\tau = - \int \Psi S \cdot d\sigma$$

and every cut Q_m makes two contributions to the surface integral which differ formally only in the directions of the inner normals $d\sigma_1$ and $d\sigma_2$. The sum of these two contributions is

$$- (\Psi_1 - \Psi_2) \int_{C_m} (S \cdot d\sigma_1) = S_{C_m} \int (S \cdot d\sigma_1) \quad (12-8)$$

The fact that the two contributions do not in general cancel each other proves that the Gauss theorem can be applied directly only to singly connected regions. According to what has been agreed to about the points 1 and 2, the normal $d\sigma_1$ has the same direction as the sense of the curves C_m .

(c) From eq. 12-1 and the fundamental equation $X: H = -c \text{ curl } G$ it follows that

$$\text{curl} (cG + A) = 0 \quad (12-9)$$

Therefore a superconduction scalar potential Ψ exists for which

$$\text{grad } \Psi = cG + A \quad (12-10)$$

As there is no supercurrent outside the superconductor this potential is defined only in the interior. The integral

$$\begin{aligned} S_C &= \int_C (ds \cdot \text{grad } \Psi) = \int_C ds (cG + A) \\ &= c \int_C G \cdot ds + \int_C A \cdot ds \end{aligned} \quad (12-11)$$

therefore has the value zero for any closed curve C in a singly connected superconductor; in a doubly connected superconductor (in the form of a ring) it is likewise zero for curves of the first kind, but has in general a unique value S_{C_2} different from zero. In an n -ply connected superconductor the integral has the same value S_{C_m} for all curves of the m^{th} kind. The superconduction potential Ψ is multiple valued ("periodic") with the "periods" S_{C_m} .

We differentiate eq. 12-10 with respect to time and use the fundamental equation IX ($E = \partial G / \partial t$) and also eq. 12-2 to obtain

$$-c \text{ grad } \Phi = \text{grad } \frac{\partial \Psi}{\partial t} \quad (12-12)$$

The potential Φ is defined in all space, and is therefore unique. Integrating eq. 12-12 over a closed curve C_m within the superconductor:

$$\frac{d}{dt} \int_{C_m} (ds \cdot \text{grad } \Psi) = \frac{dS_{C_m}}{dt} = 0 \quad (12-13)$$

The integrals S_C do not change with time so long as the specimen remains superconducting. This is still true if during a phase transition the superconducting material grows at the expense of the normal material so causing the ring to become thicker, or, if it shrinks, by the reverse process.

The explanation of the persistent current contained in these theorems is due to F. London.

All experiments on the persistent current have been done with doubly connected superconductors, e. g., in the form of a ring or a closed coil. Moreover, the superconductor has always been thick compared with the penetration depth. If the curve C_2 be placed in the field-free interior, $G = 0$ on the curve and it follows from eq. 12-11 that

$$S_C = \int_C B \cdot d\sigma \quad (12-14)$$

From this eq. 12-13 shows that the flux of induction through any surface that encloses the bore of the ring and protrudes through the protective layer into the field free interior (which adds but little) is constant, see Fig. 12-3.

Therefore if a ring has been placed in a magnetic field while still above its transition temperature, and if on cooling below the transition a certain flux of induction is trapped in the bore of the ring, this will remain there until superconductivity is destroyed: it is "frozen in." If the external field

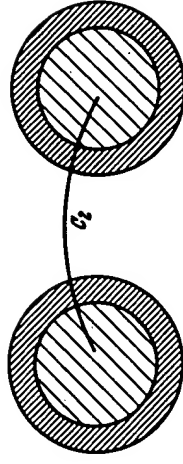


Fig. 12-3. Illustrating a curve C_2 lying entirely within the field-free bore of a ring. Darkly shaded area represents the protective layer; lightly shaded area represents the protected interior.

is switched off, the ring acts as a permanent magnet due to this flux of induction. The great achievement of the London theory is that it logically combines this freezing-in process with the Meissner effect, i. e., the fact that the field inside a superconductor does not get frozen in but is expelled. If a superconducting ring initially free of current is placed in a magnetic field, the lines of force will go around it according to eq. 12-14; its bore remains permanently field free.

It should be emphasized once more that eq. 12-14 holds only for "thick" rings; for "thin" ones the line integral in S_C (eq. 12-11) cannot be neglected. In such rings the flux of induction does not freeze in. Immediately below the transition temperature every specimen is effectively thin, as has been repeatedly pointed out. The flux which according to eq. 12-14 remains constant, is not necessarily identical with the flux that passed through the bore before the ring became superconducting.

The ohmic current has not been mentioned in the above discussion. This does not mean that it is zero under the circumstances of the problem, or that we have neglected it. On the contrary our conclusions are completely rigorous and independent of what happens to the ohmic current during the changes under consideration. Strictly speaking, the ohmic current has always to play its role as consumer of energy during the processes, the more strongly the more rapid the process. The fact that nothing of this kind can be detected in actual experiments, is due to the relatively slow rate of change at practicable frequencies.²

²In multiply connected specimens carrying a persistent current the superconduction potential is certainly not zero everywhere, according to the argument in the text. However, we may ask whether perhaps it does not vanish identically for a singly connected superconductor in a static magnetic field? This question has to be answered in the negative, in so far as we understand by A the potential introduced in (a) and describing the total *magnetic* field. This can already be seen for the cubic crystal where especially simple conditions prevail because \mathbf{J} and \mathbf{G} have the same directions. Owing to eq. 12-10 and the boundary condition $\mathbf{J}_n = 0$ (and therefore also $\mathbf{G}_n = 0$) we must have

$$\frac{\partial \Psi}{\partial n} = A_n$$

and it is certainly not generally true that $A_n = 0$. However, by relinquishing the representation of the *whole* field, we could introduce a potential for the interior of the superconductor alone:

$$A' = A - \text{grad } \Psi$$

$$c(\mathbf{t} + A') = 0$$

For this potential we should have

Equation 12-1 would be retained in the form $\mathbf{H} = \text{curl } A'$. Whereas according to eq. 12-3 $\text{div } A = 0$ for stationary fields generally, the relation $\text{div } A' = 0$ would follow from eq. 12-10 only for cubic crystals. It is only for these crystals that the equation $\text{div } \mathbf{G} = 0$ follows from $\text{div } \mathbf{J} = 0$. Because of this restriction, no special significance can be attached to the potential A' .

(d) Let us calculate the "period" of the superconduction potential

$$S_C = \int \mathbf{H} \cdot d\sigma = 2\pi \int_0^\infty r \mathbf{H}_i dr$$

in the example of a hollow cylinder of cubic crystal material, with an inner radius R and field H_i in the interior hollow space [Chap. 9 (a)]. The integral with respect to r should extend as far as a circle situated in the protected field-free space inside the superconductor. This is expressed in the formula by writing the upper limit as infinite.

Now for $r < R$, $\mathbf{H}_i = H_i$, whereas for $r > R$, according to eq. 10-7

$$\mathbf{H}_i = H_i \frac{H_0(\iota\beta r)}{H_0(\iota\beta R)}$$

so according to the theorem

$$\int_x^\infty \zeta H_0(\zeta) d\zeta = -x H_1(x)$$

we obtain

$$S_C = 2\pi R^2 H_i \left[\frac{1}{2} - \frac{1}{\iota\beta R} \frac{H_1(\iota\beta R)}{H_0(\iota\beta R)} \right]$$

The second term in the bracket is positive real, as it should be, because both $\iota H_0(\iota\beta R)$ and $-H_1(\iota\beta R)$ are also positive real. For large βR this term is vanishingly small compared with the first term because the ratio of the two Hankel functions becomes unity. For small βR , however, it becomes the dominant term, even increasing without limit as βR decreases, because $-H_1(\iota\beta R)$ becomes $2/\pi\beta R$, and $\iota H_0(\iota\beta R) \rightarrow -(2/\pi) \ln(\beta R)$ in this limit. Thus we get

$$S_C = -\frac{2\pi H_i}{\beta^2 \ln(\beta R)} \quad (12-15)$$

S_C therefore vanishes when $R = 0$ as in this case, of course, the hollow cylinder becomes a simply connected solid cylinder.

If we imagine the temperature of a given hollow cylinder to be increased, then its λ increases, and consequently β and βR decrease, approaching zero when the transition temperature T_c is reached. The factor multiplying H_i increases without limit, and since S_C remains constant, according to what has been said above, H_i must accordingly decrease. The physical reason for this is the increase in the penetration depth β^{-1} . The field penetrates the superconductor and spreads over a continuously increasing area, so its intensity has to decrease because of the constancy of the total flux S_C . The superconduction potential Ψ is proportional to the angle θ because of axial symmetry: thus

$$\Psi = \frac{\theta}{2\pi} S_C$$

and Ψ satisfies the potential equation³ $\Delta \Psi = 0$. This must be so for all stationary currents in cubic-crystal superconductors according to eqs. 12-10 and 12-3 because from $\text{div } \mathbf{i} = 0$ it follows for such crystals that $\text{div } \mathbf{G} = 0$.

(c) When there is a persistent current in a ring, it has a magnetic moment. Does the direction of the moment depend on the way in which it has been produced? This and similar questions are answered by the uniqueness theorem for a superconductor in a stationary field. We derive it now under the assumption that no ohmic current is supplied from outside.

We form the scalar product of 12-10 with $\mathbf{i}/2c$, and integrate over the volume of an arbitrary (homogeneous or inhomogeneous) superconductor as indicated by the suffix s under the integral sign. This yields

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau = \frac{1}{2c} \int_s (\mathbf{i} \cdot \text{grad } \Psi) d\tau \quad (12-16)$$

Using the formula

$$(\mathbf{i} \cdot \text{grad } \Psi) + \Psi \text{div } \mathbf{i} = \text{div } (\Psi \mathbf{i})$$

the right-hand integral in eq. 12-16 can be transformed into

$$-\frac{1}{2c} \int_s (\Psi \text{div } \mathbf{i}) d\tau - \frac{1}{2c} \int_s \Psi (\mathbf{i} \cdot d\sigma)$$

Now because of the assumed stationary conditions in the interior, the fundamental eq. VI becomes $\text{div } \mathbf{i} = 0$, and at the surface eq. 3-7 gives $\mathbf{i} \cdot \mathbf{n} = 0$. Therefore nothing remains of the above expressions except the contribution of the cross-sectional cuts which eventually have to be introduced. For the time being we assume the superconductor to be doubly connected so we need only one cut. By eq. 12-8 its contribution is

$$-\frac{1}{2c} (\Psi_1 - \Psi_2) \int_0^1 \mathbf{i} \cdot d\sigma_1 = \frac{1}{2c} S_c \int_0^1 \mathbf{i} \cdot d\sigma_1 \quad (12-17)$$

We write

$$\int_0^1 \mathbf{i} \cdot d\sigma_1 = I_s \quad (12-18)$$

the current in the ring. As $d\sigma_1$ is in the same direction as the curves C_1 , I_s is positive if the current flows in the same sense as C_2 , otherwise it is negative. Equation 12-16 is transformed in this way into

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau = \frac{S_c I_s}{2c} - \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau \quad (12-19)$$

On the other hand, the magnetic energy of the field is, by eqs. 5-8 and 3-2

$$\frac{1}{2} \int_s \mu \mathbf{H}^2 d\tau = \frac{1}{2} \int_s (\mathbf{H} \cdot \mathbf{B}) d\tau - \frac{1}{2} \int_s (\mathbf{H} \cdot \mathbf{M}) d\tau$$

³ θ is the imaginary part of the complex function $\ln(x + iy)$.

where the suffix V indicates that the integral extends over the whole of space, whereas the suffix P indicates that it extends over only the permanent magnets in the field. By eq. 12-1 and the rule 5-1 we have

$$\frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{B}) d\tau = \frac{1}{2} \int_V (\mathbf{H} \cdot \text{curl } \mathbf{A}) d\tau = \frac{1}{2} \int_V (\mathbf{A} \cdot \text{curl } \mathbf{H}) d\tau - \frac{1}{2} \int_V ([\mathbf{A} \times \mathbf{H}] \cdot d\sigma)$$

The surface integral vanishes over the sphere at infinity because there \mathbf{H} behaves like R^{-3} . The tangential components of \mathbf{H} and \mathbf{A} are continuous at surfaces of discontinuity, therefore the normal component of $[\mathbf{A} \times \mathbf{H}]$ which depends only on these tangential components is also continuous and does not contribute anything. Therefore

$$\frac{1}{2} \int_V \mu \mathbf{H}^2 d\tau = \left(\frac{1}{2c} \right) \int_V (\mathbf{A} \cdot \mathbf{i}) d\tau - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-20)$$

The field is produced by the ohmic current in the normally conducting coils together with the corresponding supercurrent in the superconductor, and also by any persistent current that may be present. We designate the coils by the suffix c under the integral sign. Splitting up the right-hand side of eq. 12-20 in this way yields:

$$\frac{1}{2} \int_V \mu \mathbf{H}^2 d\tau = \frac{1}{2c} \int_s (\mathbf{A} \cdot \mathbf{i}) d\tau + \frac{1}{2c} \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau$$

Adding this equation to 12-19 we get

$$\frac{1}{2} \int_s (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int_V \mu \mathbf{H}^2 d\tau = \frac{1}{2c} \left\{ S_c I_s + \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau \right\} - \frac{1}{2} \int_P (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-21)$$

According to eq. 5-8 the left-hand side of this is the total energy of the field U , which is necessarily positive or zero, the latter only if $\mathbf{i} \cdot \mathbf{n} = 0$ and $\mathbf{H} = 0$ everywhere. This equation implies the following theorem.

The "period" S_c of the superconduction potential in the ring, together with the ohmic currents and the permanent magnets determine uniquely the magnetic field of the supercurrent. This is because if we assume two different fields with the same ohmic currents and permanent magnets, the difference between the two fields also satisfies the differential equations of the London theory. Therefore eq. 12-21 may be expressed in terms of this difference, but the right-hand side vanishes by hypothesis.

For a singly connected superconductor the first term of the right-hand side is missing; it is therefore current free in the absence of external excitation; otherwise the apparatus producing the field determines the situation uniquely. This theorem also guarantees the uniqueness of the solution of those examples in Chaps. 10 and 11 which are not covered already by the uniqueness theorem of eq. 7-4. Equation 12-21 admits the possibility of an independent persistent current in a ring, but otherwise the ring is determined in all details by specifying its S_c . For instance its

magnetic moment is equal to $Sc \mathbf{P}$ where \mathbf{P} is a vectorial factor depending only on the geometry of the ring and the intensive functions of position λ, ρ . The magnetic moment can only assume two opposite directions; the sign of Sc decides which one. In so far as the persistent current alone is exciting the field, the direction of the current is such as to make $Sc \mathbf{i}$ positive. If as in Fig. 12-1 the current flows in the positive sense, assigned to all curves C_2 in the ring, then the magnetic lines of force that pass through the ring have the direction of $d\sigma$, i. e., they come toward the reader. If we place a ring carrying a persistent current in an additional external magnetic field, then an induced current is superposed on the original current. In spite of the constancy of Sc the resulting current strength \mathbf{i} can become zero or even reverse in sign.

Let a normally conducting specimen be placed in a magnetic field and then cooled down until it becomes superconducting; then there is a considerable flux of induction through the ring but no current, or only a very weak current. Which of these possibilities is realized depends upon the detailed course of events during the cooling process and is difficult to determine. Switching off the magnetic field does not change the flux, but the current increases to the strength determined by the total flux and the form of the specimen. This is a common method of producing persistent currents.

To generalize eq. 12-21 for an n -ply connected superconductor we replace the one term $Sc \mathbf{i}$ by $(n-1)$ terms of the same kind. The corresponding statement applies if several separate superconductors are present in the field.

Because of its magnetic moment every superconductor that has a persistent current must experience a torque in a homogeneous magnetic field in addition to that due to field deformation caused by the shape of the specimen.⁴

(f) Let us assume two superconductors, both with persistent currents I and I' , to be moving relative to each other. The forces between them perform work, and for lack of any other source of energy, at the expense of the energy $Sc I + Sc' I'$. Because Sc and Sc' are constants according to eq. 12-14 a change of energy is only possible by a change of the strengths of the currents.

Suppose the superconductors to be rings formed by circles rotated around axes of symmetry that do not intersect the circles (Fig. 12-4). Let them be in such a relative position that at first they are at a great distance from each other and their axes of symmetry coincide. In this situation let the

⁴Why is it that there is in the theory of ohmic currents and their magnetic fields, no uniqueness theorem corresponding to eq. 12-21? This is because in this case the question of current distribution is answered uniquely by electrostatics and because after solving this problem the magnetic field can be deduced unambiguously from the current density. It is impossible to separate the problem of the superconductor into two parts in this way.

current I flow in the first ring, but zero current in the second one. Let the rings now be brought together. The resulting lines of force are then as sketched diagrammatically in the figure. If the current I flows away from the reader on the right-hand side (at the minus sign), then the current in the second ring flows toward the reader on the right-hand side. This follows from the rule [Chap. 7 (c)] that inner normal of the conductor, current, and magnetic field form a right-handed system. The antiparallel currents I_1 and I_2' repel each other; bringing the rings together requires the performance of work and produces an increase of the field energy $Sc_1 I_1$, and thus an increase of I_1 . However I_2' is also increased because the lines of force crowd together near the second ring and create a greater field strength the smaller the distance.

If a current I_3^0 is initially flowing in the second ring when at infinite separation, then the current $I_3^0 - I_2$ flows at the smaller distance, and there is attraction or repulsion depending on whether this expression is positive or negative. We have a stable equilibrium, at least with respect to motion along the axis, because a further approach leads to repulsion, and increase of distance to attraction. For example, in Justi's persistent current electromagnet the current strength decreases when it is attracting iron and the flux of induction S remains constant [Chap. 1 (b)].

(g) A famous experiment performed in 1924 is in apparent contradiction to this argument. Kamerlingh-Onnes⁵ excited a persistent current in a hollow sphere of lead and so apparently in a singly connected region. He produced the current by the usual method of bringing the specimen, while at a higher temperature, into a magnetic field and then cooling it to become superconducting. The sphere showed a magnetic moment after removing the field and experienced the corresponding torque in any external field. This great investigator concluded that the paths of the current could not be displaced in the superconducting body. If they could be, the forces exerted by the external field would be unable to move the sphere because it has no preferential direction.

From later experience the following explanation can be given for the above observation. The cooling of the hollow sphere immersed in liquid helium did not proceed everywhere with the same speed. At first one or may be several annular zones became superconducting while the rest of

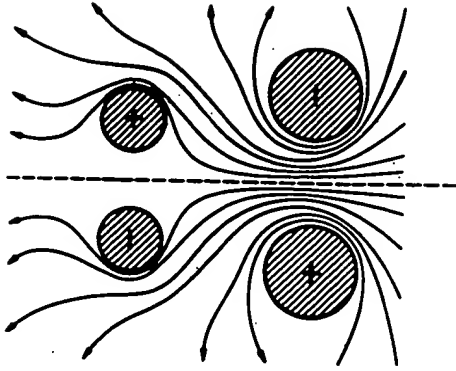


Fig. 12-4. Two superconducting rings with magnetic field lines.

⁵H. Kamerlingh-Onnes, *Commun. Leiden Supplement*, 50a, (1924).

the sphere remained normal. With the approach of temperature equilibrium the whole sphere had not become superconducting; instead, after the first zone had once trapped a certain amount of flux, the latter remained unchanged in the nonsuperconducting remainder of the sphere which stayed in the intermediate state (Chap. 19). With increasing concentration of the lines of force as the annular ring of superconducting material grew and the cross section of the normal material decreased, the field strength increased finally beyond the critical value H_c in the rest of the sphere and so prevented the complete establishment of the superconducting state.

Actually therefore the supercurrent was flowing in one or in several rings. Its magnetic moment was attached rigidly to this ring, and therefore also to the sphere, so the latter was forced to orient itself in an external field. This follows inevitably from the uniqueness theorem. However, even though Kamerlingh-Onnes failed to interpret his experiments, his question whether the current lines are displaced in a superconductor under the influence of an external magnetic field is still perfectly legitimate. This is discussed in Chap. 13.

(h) In the examples discussed in the last paragraph and in section (d) it was assumed that no ohmic current was supplied to the doubly connected superconductor from outside. But now let us imagine that at two points a and b on the surface of the superconductor, normally conducting wires are soldered through which a current I is supplied, entering at a and leaving at b , see Fig. 12-5. The ohmic current is distributed through the superconductor with a current I' flowing in the path that goes from a to b in the same direction as the "sense" of the ring (which we arbitrarily choose once for all from "2" to "1"), and a current I'' in the other path. We regard both currents as positive if they are flowing from a to b . However, we know from Chap. 2 that one of them can be negative. This is true particularly if a persistent current is superimposed on the supplied current. In general

$$I' + I'' = I \quad (12-22)$$

This modified assumption does not alter eq. 12-10. Therefore eqs. 12-11 and 12-13 together with the theorems derived from them remain valid. But the integral on the right-hand side of eq. 12-16

$$\int (\mathbf{i} \cdot \text{grad } \Psi) d\tau = - \int \Psi (\mathbf{i} \cdot d\sigma)$$

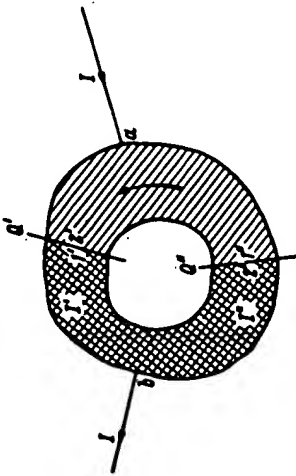


Fig. 12-5. Superconducting ring with normally conducting leads. The arrow shows the "sense" of the ring and also the positive I' current direction. A positive current I'' flows in the opposite direction. The sense of the ring is from 2' to 1' and from 2'' to 1''.

(h) In the examples discussed in the last paragraph and in section (d) it was assumed that no ohmic current was supplied to the doubly connected superconductor from outside. But now let us imagine that at two points a and b on the surface of the superconductor, normally conducting wires are soldered through which a current I is supplied, entering at a and leaving at b , see Fig. 12-5. The ohmic current is distributed through the superconductor with a current I' flowing in the path that goes from a to b in the same direction as the "sense" of the ring (which we arbitrarily choose once for all from "2" to "1"), and a current I'' in the other path. We regard both currents as positive if they are flowing from a to b . However, we know from Chap. 2 that one of them can be negative. This is true particularly if a persistent current is superimposed on the supplied current. In general

$$I' + I'' = I \quad (12-22)$$

This modified assumption does not alter eq. 12-10. Therefore eqs. 12-11 and 12-13 together with the theorems derived from them remain valid. But the integral on the right-hand side of eq. 12-16

$$\int (\mathbf{i} \cdot \text{grad } \Psi) d\tau = - \int \Psi (\mathbf{i} \cdot d\sigma)$$

acquires another value because it is no longer true that $\mathbf{i} \cdot \mathbf{e} = 0$ everywhere over the surface. Suppose the cut that contributes to the integral is made first in the branch carrying the current I' ; this cut may be called Q' and the function Ψ for this case will be written Ψ' . The integral then becomes

$$-(\Psi'_a - \Psi'_b) I + S_c I'$$

If we displace the cut to the other branch and call it Q'' , and the corresponding function Ψ'' , the surface integral becomes in the same way

$$-(\Psi''_a - \Psi''_b) I - S_c I''$$

Here I'' has a minus sign because a positive I'' has, by hypothesis, a direction opposite to the sense of the ring. The two values are equal because their difference

$$[(\Psi'_a - \Psi'_b) - (\Psi''_a - \Psi''_b)] I - (I' + I'') S_c = 0$$

This can be seen in the simplest way from eq. 12-22 by making use of the undetermined additive constant in the definition of Ψ to make $\Psi'_a = \Psi''_a$. In this case Ψ' and Ψ'' are equal throughout the whole singly shaded region in Fig. 12-5 between the two cuts that enclose the point a whereas in the other cross-hatched area between the two cuts enclosing the point b we have $\Psi'' - \Psi' = S_c$. Equation 12-21 is now replaced either by

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int_V \mu \mathbf{H}^2 d\tau = \frac{1}{2c} [(\Psi'_b - \Psi'_a) I + S_c I' + \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau] - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (12-23)$$

or by

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) d\tau + \frac{1}{2} \int_V \mu \mathbf{H}^2 d\tau = \frac{1}{2c} [(\Psi''_b - \Psi''_a) I - S_c I'' + \int_c (\mathbf{A} \cdot \mathbf{i}) d\tau] - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau$$

the term containing S_c has the positive or negative sign if the current is in the positive sense I' or the negative sense I'' respectively. This agrees with the sign of the corresponding term in eq. 12-21.

This alteration does not affect the uniqueness theorem which we linked with eq. 12-21 because the current I supplied to the superconductor belongs to the ohmic currents of the external field. Also I becomes zero for the difference field between two fields corresponding to the same "period" S_c , the same ohmic currents, and the same permanent magnets.

(i) Considered as the source of its field, a persistent current has, according to eq. 12-21, only the energy $U = S_c I^2$. However, S_c is proportional to I^2 , and we may write

$$\frac{S_c}{c} = p^2 I^2 \quad (12-24)$$

and we see from the equation

$$U = \frac{1}{2} p^{ss} I^2 \quad (12-25)$$

that p^{ss} is the coefficient of self-induction of the superconducting ring. It differs from the self-induction for an ohmic current in that in U and therefore also in p^{ss} there is a positive term due to the energy of the supercurrent. However, this term is usually quite insignificant compared with the magnetic energy, because the superconductivity occurs for the most part only in thin layers where, due to the continuity of the components of \mathbf{H} , most of the energy density is of the same order of magnitude as in adjoining parts of the outside space (see eq. 7-37). This positive contribution is annulled in thick specimens by the far greater negative contribution from the expulsion of the field.⁶ This idea can be carried through quantitatively only for special cases because the external magnetic field outside a superconductor is generally different from that for an ohmic conductor.

From eqs. 12-14 and 12-24 it follows that for a thick superconductor the coefficient of self-induction is equal to the flux through its own current circuit divided by the velocity of light c and the current strength. For thin superconductors there is a correction according to eq. 12-11. It is well known that this theorem does not hold for normal conductors, because it is then impossible to define the flux through its own current circuit in so far as the latter is considered to have extension in space, whereas if it is considered infinitely thin, the flux is no longer finite.

If there are ohmic currents of strength I^e present in addition to the persistent current, we get

$$S_C = p^{ss} I^s + \sum_e p^{se} I^e$$

a linear function of all the current strengths. Furthermore, because the vector potential \mathbf{A} is a linear sum of all the contributions from the separate currents, eq. 12-21 gives for the field energy, omitting the magnetic contribution,

$$U = \frac{1}{2} \sum_{ik} p^{ik} I_i I_k$$

This summation is extended over all the ohmic currents as well as the persistent current. The coefficients of induction between the persistent current and the ohmic currents are also affected by the energy of the supercurrent in the same way as the self-induction p^{ss} . Beyond this we can say nothing without further information about the effect of the expulsion of the field.

⁶However, in a cable with the return path formed by its shell at a small distance from the inner conductor, supposing the shell to be superconducting, the superconductivity energy could be responsible for almost one-half of the coefficient of self-induction.

With regard to the other coefficients, the self-induction and the mutual inductions between the ohmic currents are also affected by the presence of the superconductor, just as they depend on the magnetic permeability in their neighborhood. One method for measuring the penetration depth β^{-1} and the constant λ is based on this fact. It was devised by Casimir⁷ and used with success by Laurmann and Shoenberg⁸; although not absolute, it gives the dependence on temperature. A long solenoid is wound around a superconducting cylinder and a shorter induction coil is wound tightly around its center; their mutual induction is measured. The greater the penetration depth, the greater the flux of induction through the measuring coil due to the long solenoid, and so the greater their mutual induction. Two different specimens of mercury gave slightly different results in this experiment, and this is a reminder of the fact that the constant λ is really a tensor.

CHAPTER 13

The Maxwell and London Stresses

(a) Kamerlingh-Onnes in 1924 raised the question whether the track of the supercurrent could be displaced in the superconductor under the influence of an external magnetic field [see Chap. 12 (g)]. He started from the assumption that in any case in the steady state the carriers of the supercurrent do not experience any forces due to the material itself, i. e., to the atoms and the carriers of the ohmic current, for otherwise persistent currents would be impossible. His question was, however, inconsequential in so far as the supercurrent already has its own magnetic field, so that the problem exists even before any external field enters the picture. Our present ideas about the current distribution had not been developed in 1924. We now have a clear picture of the current concentration in the protecting layer and we know that the current, magnetic field, and the inner normal to the surface form a right-handed system (Chap. 7), and therefore that the force per unit volume $\frac{1}{2} [\mathbf{j} \times \mathbf{H}]$ due to its own magnetic field is directed toward the interior of the superconductor (current, field, and force also form a right-handed system). We may therefore raise the question: Why does the magnetic field not push the current into the interior? How can the current in the thin protecting layer have any stability at all?

Another question is intimately connected with this. A rod carrying a supercurrent I and located in a magnetic field H perpendicular to the axis of the cylinder, experiences a force $\frac{1}{2} I H$ per unit length. Upon what does this force act? If the supercurrent mechanism experiences no force

⁷H. G. B. Casimir, *Physica*, 7, 887 (1940).

⁸E. Laurmann and D. Shoenberg, *Nature*, 160, 747 (1948).

due to the material, neither can it exert force on the material: action and reaction must be equal. And yet the force due to the magnetic field certainly has to act first on the supercurrent mechanism, and through this somehow on the rod.

The answer can only be that the forces act on the material discontinuity at the surface. It is there that the interaction between matter and the supercurrent carriers must be located, and not in the interior. If such forces were not present even at the surface, the carriers would be able to escape from the metal, which certainly does not happen. The theory answers all these questions in terms of the London stresses. The force ordinarily exerted by the field can be calculated from the divergence of the Maxwell stresses, which are defined in terms of the electric and magnetic fields; similarly the London stresses, which depend only on the supercurrent, take care of the force exerted by the magnetic field on the supercurrent mechanism, and in fact locate it at the surface instead of throughout the body of the material. The supercurrent hangs as it were from the surface like a curtain, the magnetic field of the current corresponds to the weight of the curtain, the London stresses correspond to the elastic forces holding the curtain to its curtain rod and prevent it from falling into the interior. This is how we can answer Kamerlingh-Onnes' question.

The point therefore is to find a stress tensor that depends only on the current density \mathbf{i} and that has a divergence that everywhere just compensates the force resulting from the Maxwell stresses in the magnetic field.¹ London's fundamental equations IX and X are needed to carry this through mathematically. They enter as the necessary and sufficient conditions for the system of London stresses to just compensate the Maxwell forces. The whole current distribution is fixed by this equilibrium condition. We regard the fact that it makes such a compensation possible as inherently the strongest point in favor of the theory.

This compensation is not entirely necessary for inhomogeneous superconductors or non stationary currents. The discussion of the general equation 13-10 actually leads to completely new points of view.

(b) To begin with we define nine quantities in terms of two arbitrary vector functions of position \mathbf{P} and \mathbf{Q} :

$$\Theta_{\alpha\beta}(\mathbf{P}, \mathbf{Q}) = \mathbf{P}_\beta \mathbf{Q}_\alpha - \frac{1}{2} \delta_{\alpha\beta} \sum_\gamma \mathbf{P}_\gamma \mathbf{Q}_\gamma \quad (\alpha, \beta = 1, 2, 3) \quad (13-1)$$

They form the components of a tensor of the second rank because the two parts $\mathbf{P}_\beta \mathbf{Q}_\alpha$ and $\frac{1}{2} \delta_{\alpha\beta} \sum_\gamma \mathbf{P}_\gamma \mathbf{Q}_\gamma$ are each tensors themselves.² Written in greater detail the definition 13-1 reads:

$$\begin{aligned} \Theta_{11}(\mathbf{P}, \mathbf{Q}) &= \frac{1}{2} (\mathbf{P}_1 \mathbf{Q}_1 - \mathbf{P}_2 \mathbf{Q}_2 - \mathbf{P}_3 \mathbf{Q}_3) \\ \Theta_{23} &= \mathbf{P}_3 \mathbf{Q}_2, \quad \Theta_{32} = \mathbf{P}_2 \mathbf{Q}_3, \quad \text{etc.} \end{aligned} \quad (13-2)$$

¹As we later put $-\text{div } \Theta$ equal to the force acting on the material we have to regard a positive $\Theta_{\alpha\alpha}$ as a pressure, a negative one as a tension.
² $\delta_{\alpha\beta} = 1$ for $\alpha = \beta$, otherwise zero.

We now form the divergence of this tensor, i. e., the vector of which the x_1 component is³

$$\text{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \frac{\partial \Theta_{11}}{\partial x_1} + \frac{\partial \Theta_{12}}{\partial x_2} + \frac{\partial \Theta_{13}}{\partial x_3} \quad (13-3)$$

Carrying through the calculation yields

$$\text{div}_1 \Theta(\mathbf{P}, \mathbf{Q}) = \mathbf{Q}_1 \text{div } \mathbf{P} - [\mathbf{P} \times \text{curl } \mathbf{Q}]_1 + \frac{1}{2} \left(\sum_\gamma \mathbf{P}_\gamma \frac{\partial \mathbf{Q}_\gamma}{\partial x_1} - \sum_\gamma \mathbf{Q}_\gamma \frac{\partial \mathbf{P}_\gamma}{\partial x_1} \right) \quad (13-4)$$

Now we set $\mathbf{P} = \mathbf{i}$, $\mathbf{Q} = \mathbf{G}$, i. e., $\mathbf{Q}_\alpha = \sum_\beta \lambda_{\alpha\beta} \mathbf{i}_\beta$ (see eq. VIII Chap. 3); then because of the symmetry relation 3-3 ($\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$), the two sums cancel each other, at least if the $\lambda_{\alpha\beta}$ are independent of x_α . Otherwise there remains a term:

$$\frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \frac{\partial \lambda_{\alpha\beta}}{\partial x_1}$$

By writing the tensor of third rank with components $\partial \lambda_{\alpha\beta} / \partial x_\gamma$ as $\nabla(\lambda_{\alpha\beta})$, the following vector equation results:

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = \mathbf{G} \text{div } \mathbf{i} - [\mathbf{i} \times \text{curl } \mathbf{G}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla(\lambda_{\alpha\beta}) \quad (13-5)$$

Now we use the continuity equation VI and the fundamental equation X to obtain

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = -\mathbf{G} \frac{\partial \rho}{\partial t} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla(\lambda_{\alpha\beta}) \quad (13-6)$$

Finally remembering IX we write

$$-\mathbf{G} \frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial t} (\rho \mathbf{G}) + \rho \mathbf{i} \frac{\partial \mathbf{G}}{\partial t} = -\frac{\partial}{\partial t} (\rho \mathbf{G}) + \rho \mathbf{E}$$

and find in this way that

$$\text{div } \Theta(\mathbf{i}, \mathbf{G}) = \rho \mathbf{E} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla(\lambda_{\alpha\beta}) - \frac{\partial}{\partial t} (\rho \mathbf{G}) \quad (13-7)$$

On the other hand, if we form the Maxwell stress tensors $T(\mathbf{E})$ and $T(\mathbf{H})$ for the interior of the superconductor where we do not need to distinguish between \mathbf{D} and \mathbf{E} or between \mathbf{B} and \mathbf{H} , we have

$$T(\mathbf{E}) = -\Theta(\mathbf{E}, \mathbf{E}), \quad T(\mathbf{H}) = -\Theta(\mathbf{H}, \mathbf{H}) \quad (13-8)$$

Remembering the Maxwell equations I, and IV, it follows from 13-4 that

$$\begin{aligned} -\text{div } \{T(\mathbf{E}) + T(\mathbf{H})\} &= \mathbf{E} \text{div } \mathbf{E} - [\mathbf{E} \times \text{curl } \mathbf{E}] + \mathbf{H} \text{div } \mathbf{H} - [\mathbf{H} \times \text{curl } \mathbf{H}] \\ &= \rho \mathbf{E} + \frac{1}{c} [\mathbf{i} \times \mathbf{H}] + \frac{1}{c} \frac{\partial}{\partial t} [\mathbf{E} \times \mathbf{H}] \end{aligned} \quad (13-9)$$

³See previous footnote.

Here ρ is the total density $\rho^0 + \rho'$, \mathbf{i} the total current $\mathbf{i}^0 + \mathbf{i}'$. Subtracting from eq. 13-7 yields

$$-\operatorname{div} [T(\mathbf{E}) + T(\mathbf{H}) + \Theta(\mathbf{i}', \mathbf{G})] = \rho^0 \mathbf{E} + \frac{1}{c} [\mathbf{i}^0 \times \mathbf{H}] - \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla (\lambda_{\alpha\beta}) + \frac{\partial}{\partial t} \left\{ \frac{1}{c} [\mathbf{E} \times \mathbf{H}] + \rho' \mathbf{G} \right\} \quad (13-10)$$

This equation constitutes the momentum law.

In the stationary state \mathbf{E} and \mathbf{i}^0 vanish (Chap. 7), and for the homogeneous body the double sum vanishes. In the stationary state, the Maxwell stresses of the magnetic field and the London stresses of the supercurrent result in no net force on the interior of a homogeneous superconductor, as was required. The symmetry of the tensor $\lambda_{\alpha\beta}$ is found to be a necessary and sufficient condition for this. In a time-dependent field the ohmic current mechanism exerts the force $\rho^0 \mathbf{E} + (1/c) [\mathbf{i}^0 \times \mathbf{H}]$ per unit volume; it serves to change the mechanical momentum density. Moreover, the forces due to the three stress tensors produce an increase in the well-known electromagnetic momentum $(1/c) [\mathbf{E} \times \mathbf{H}]$ and of the momentum density of the supercurrent $\rho' \mathbf{G}$. (This is why we have called \mathbf{G} the supermomentum.) Discussion of the double sum in eq. 13-10 is deferred until later. This also shows why we were not permitted to put the superconduction charge density ρ' equal to zero even in the stationary state where ρ is zero (see Chaps. 4 and 5): the momentum $\rho' \mathbf{G}$ is without doubt always present in the stationary current.

(c) The Maxwell stresses do not act on the surface of a superconductor except in the case (not to be discussed here) that the material immediately across the surface has a dielectric constant or a permeability differing from unity. As all the components of \mathbf{E} and \mathbf{H} are continuous across the boundary, according to the boundary conditions of Chap. 3 (c), the tensors $T(\mathbf{E})$ and $T(\mathbf{H})$ have equal components on either side of the surface, and so have no "surface divergence." However, the London tensor $\Theta(\mathbf{i}', \mathbf{G})$ does have a surface divergence because the supercurrent ceases at the surface. Let $\mathbf{P}_{(n)}$ be this negative surface divergence, the \mathbf{n} referring to the inner normal of the surface; its components are

$$\mathbf{P}_{(n)\alpha} = - \sum_{\beta} \Theta_{\alpha\beta} \cos(n, x_{\beta}) \quad (13-11)$$

Using the definition 13-1 and introducing the unit vector \mathbf{n} in the direction \mathbf{n} , we can write vectorially

$$\mathbf{P}_{(n)} = -\mathbf{i}_n \mathbf{G} + \frac{1}{2} (\mathbf{i}' \cdot \mathbf{G}) \mathbf{n} \quad (13-12)$$

$\mathbf{P}_{(n)}$ is the force exerted by the supercurrent on the surface per unit area. This is the only ponderomotive force exerted by the current.

Wherever there is no current entering (or leaving) across the surface, $\mathbf{i}_n = 0$, a tension $\frac{1}{2} (\mathbf{i}' \cdot \mathbf{G})$ acts toward the interior. At points where

current enters there is a tangential component of the force due to the first term in 13-12.

In cubic crystals, $\mathbf{G} = \lambda \mathbf{i}'$ has the same direction as \mathbf{i}' everywhere. Then the current streamline is the only intrinsic direction and must be a principal axis of the tensor $\Theta(\mathbf{i}', \mathbf{G})$. As can be seen from the equations

$$\Theta_{11} = \frac{1}{2} \lambda \{i_1'^2 - i_2'^2 - i_3'^2\}; \quad \Theta_{23} = \Theta_{32} = \lambda i_2' i_3' \quad (13-13)$$

this tensor becomes symmetrical. Putting the x_1 axis parallel to the current, the components $\Theta_{\alpha\beta}$ with mixed suffixes vanish and we get

$$\Theta_{11} = \frac{1}{2} \lambda i_1'^2, \quad \Theta_{22} = \Theta_{33} = -\frac{1}{2} \lambda i_1'^2 \quad (13-14)$$

In this case therefore a pressure $\frac{1}{2} \lambda i_1'^2$ acts along the current line, and an equal tension perpendicular to it. It manifests itself at the surface where $\mathbf{i}_n = 0$ as a tension $\frac{1}{2} \lambda i_1'^2$ directed toward the interior.

We can illustrate the meaning of the double sum in eq. 13-10 for the cubic crystal case where it reduces to

$$-\frac{1}{2} i_1'^2 \operatorname{grad} \lambda \quad (13-15)$$

Where two superconductors with different λ 's make contact, the stresses give rise to a force on the boundary. In case the current crosses the boundary perpendicularly, $(\mathbf{i}_n')_1 = (i_1')_2$ and eq. 13-15 gives the difference between the two pressures along the current lines: $\frac{1}{2} i_1'^2 (\lambda_1 - \lambda_2)$. Where, however, the two currents flow parallel to the boundary, $\lambda_1 (i_1')_1 = \lambda_2 (i_1')_2 = C$ according to eq. 3-9, and the integral of eq. 13-15 over the thickness of the boundary layer yields the difference between the two tensions: $\frac{1}{2} C^2 (1/\lambda_2 - 1/\lambda_1)$.

In all these cases the force given by eq. 13-15 is directed toward the better superconductor, with the smaller λ .

(d) The stress system assumes a particularly simple form in the fully developed protective layer of a thick cubic crystal conductor. With the z axis of coordinates along the inner normal, eqs. 7-9 and 7-10 give

$$\mathbf{H}_x = \mathbf{H}_y = 0, \quad \mathbf{i}_x' = \mathbf{i}_y' = 0, \quad \mathbf{H}_z = \sqrt{\lambda} \mathbf{i}_z'$$

Therefore in the z direction the pressure $\frac{1}{2} \mathbf{H}^2$ of the magnetic field and the tension $\frac{1}{2} \lambda i_1'^2$ of the current cancel each other at every point. In the direction of the current, however, the pressure $\frac{1}{2} \mathbf{H}^2$ and $\frac{1}{2} \lambda i_1'^2$ are equal and have to be added together, but because they do not depend on z they give rise to no resultant force, in agreement with eq. 13-10.

(e) To answer a question remaining from section (a) we now calculate from the London stresses the force exerted on a superconducting cylinder of cubic crystalline material carrying a current I in a transverse magnetic field H^0 . Figure 13-1 represents a cross section of the cylinder, and if H^0 is in the x direction, the current produced by this field flows toward the reader at a and away from the reader at b . If the current I flows toward the reader, the current at a is greater than that at b . The stronger inward

tension at a and its neighborhood results in a force from a toward b , in the y direction in the figure. This force, the current I , and the field H^0 form a right-handed system as they should.

The numerical calculation can be carried out by the methods of Chap. 8 (a) and Chap. 10 (c). From eq. 8-9 the density of the current I at $r = R$ is

$$i_r^{(1)} = \frac{\epsilon \beta I I_0 (\epsilon \beta R)}{2 \pi R I_1 (\epsilon \beta R)}$$

The current density due to the field H^0 according to eq. 10-16 is

$$i_r^{(2)} = \frac{2 \epsilon H^0 \sin \theta I_1 (\epsilon \beta R)}{\sqrt{\lambda} I_0 (\epsilon \beta R)}$$

The inward tension therefore has the strength

$$\frac{1}{2} \lambda (i_r^{(1)} + i_r^{(2)})^2$$

If this is multiplied by $-\sin \theta$, we obtain its contribution to the total force on the surface K_y , the value of which is

$$K_y = -\frac{1}{2} R \lambda \int_0^{2\pi} \int_0^{2\pi} (i_r^{(1)2} + i_r^{(2)2} + 2 i_r^{(1)} i_r^{(2)}) \sin \theta d\theta$$

Because $\int_0^{2\pi} \sin \theta d\theta = \int_0^{2\pi} \sin^2 \theta d\theta = 0$ and $\int_0^{2\pi} \sin^2 \theta d\theta = \pi$, this reduces

$$K_y = -R \lambda \int_0^{2\pi} i_r^{(1)} i_r^{(2)} \sin \theta d\theta = \frac{I H^0}{c}$$

(f) An example of the tangential component of the force K would be given by a Barlow's wheel made of superconducting cubic crystal material. This consists of a circular disk in a magnetic field parallel to its axis that would be homogeneous in the absence of the disk; current is supplied through the axis of the disk and is drawn off through a normal conductor at its perimeter. If the disk is thick compared with the penetration depth, the field is distorted by the Meissner effect and considerably increased at the periphery, while according to Chap. 7 (g) the field would penetrate a thin disk relatively undisturbed, assuming it still to be of cubic crystalline structure.

The above stresses act on the two circular faces of the disk. Because they are parallel to the axis they produce no angular momentum. However, near the point where the current leaves the disk there is a tangential current

i_θ flowing along the periphery which is proportional to H^0 and protects the interior of the (thick) superconductor from the field. At the point where the current leaves, there is a tangential force $\Theta_{\theta\theta} = \lambda i_r i_\theta$, that does produce angular momentum. The calculation shows that with a thin disk the force has the same value as for a normal conductor, while with a thick disk it has the same direction but is much weaker.⁴

The reality of the Maxwell stresses in empty space is vouchsafed by the principle of relativity. In so far as the energy density has reality in all inertial systems connected by a Lorentz transformation, the same reality must be ascribed to the stress components that are transformed along with this energy density and form with it a "world tensor." It is difficult to believe that this does not also hold for the Maxwell stresses. However, it is not inconceivable that the London stresses are purely a convenient mathematical fiction. In what follows we assume the contrary.

(g) Because in the above examples the net force and the torque are acting on an essentially rigid body, we could have started from the external magnetic stresses $T(\mathbf{H})$ instead of from the London stresses in the interior; which stresses exist in the interior is of no importance for such a calculation so long as all the stress tensors are symmetrical.

In order to carry through this alternative, we recall the two well-known integral theorems of the tensor theory: it is possible by partial integration to transform certain volume integrals of an arbitrary asymmetrical tensor $t_{\alpha\beta}$ into surface integrals. Let n again mean the inner normal, then we have first

$$\iint \left[\frac{\partial t_{11}}{\partial x_1} + \frac{\partial t_{12}}{\partial x_2} + \frac{\partial t_{13}}{\partial x_3} \right] d\tau = - \int [t_{11} \cos(n x_1) + t_{12} \cos(n x_2) + t_{13} \cos(n x_3)] d\sigma \quad (13-16)^*$$

and secondly,

$$\begin{aligned} \iint \left\{ x_2 \left(\frac{\partial t_{31}}{\partial x_1} + \frac{\partial t_{32}}{\partial x_2} + \frac{\partial t_{33}}{\partial x_3} \right) - x_3 \left(\frac{\partial t_{21}}{\partial x_1} + \frac{\partial t_{22}}{\partial x_2} + \frac{\partial t_{23}}{\partial x_3} \right) \right\} d\tau = \\ = - \int \left\{ x_2 [t_{31} \cos(n x_1) + t_{32} \cos(n x_2) + t_{33} \cos(n x_3)] - x_3 [t_{21} \cos(n x_1) + \right. \\ \left. + t_{22} \cos(n x_2) + t_{23} \cos(n x_3)] \right\} d\sigma + \int (t_{32} - t_{23}) d\tau \end{aligned} \quad (13-17)$$

⁴W. Heisenberg and M. v. Laue, *Z. Physik*, 124, 514 (1948). With regard to the present state of our knowledge about supercurrents and surface phenomena, one might perhaps doubt whether the torque is acting on the disk itself or on the normally conducting wire that leads the current out of the disk. The phenomenological theory described here cannot answer this question, but we could imagine the leads replaced by a cold emission from the periphery through the surrounding space when it could conceivably be decided experimentally whether or not the torque acts on the wheel.

* In this and subsequent formulas $d\sigma$ is not a vector.

The force per unit area on any surface due to the tensor $T(\mathbf{H})$ now has the components

$$F_{na} = \sum_{\beta} T_{a\beta} \cos(n x_{\beta}) \quad (13-18)$$

which can be written together in vector form:⁵

$$\mathbf{F}_n = -\mathbf{H}_n \mathbf{H} + \mathbf{H}^2 \mathbf{n} \quad (13-19)$$

(\mathbf{n} is again the unit vector normal).

The difference in sign between the right-hand sides of eqs. 13-18 and 13-11 is due to the fact that the Maxwell stresses we are discussing here lie outside the space element, whereas the London stresses are inside it. The resultant force on this element is, according to eq. 13-16,

$$-\int \operatorname{div} T(\mathbf{H}) d\tau = \int \mathbf{F}_n d\sigma \quad (13-20)$$

and the torque due to the Maxwell stresses is:

$$-\int [\mathbf{r} \times \operatorname{div} T(\mathbf{H})] d\tau = \int [\mathbf{r} \times \mathbf{F}_n] d\sigma \quad (13-21)^6$$

By using eq. 13-20 one can easily calculate from \mathbf{F}_n , e. g., the force $(1/c) I H^0$ acting on the cylinder carrying a current in a magnetic field treated in (c).

We now want to find the conditions under which the net force and the torque due to the Maxwell stresses in the outside space coincide with the net force and the torque due to the London stresses on the interior.

The volume integral for the Maxwell stresses on the right-hand side of eq. 13-17 vanishes because the tensor $T(\mathbf{H}) = -\Theta(\mathbf{H}, \mathbf{H})$ is symmetrical, according to eq. 13-2. It also vanishes for the tensor $\Theta(\mathbf{i}, \mathbf{G})$ in a cubic crystalline superconductor because in this case $\mathbf{G} = \lambda \mathbf{i}$. Therefore integrating eq. 13-11 over the volume of the superconductor, using eqs. 13-16 and 13-17, we conclude that

$$-\int \operatorname{div} \Theta(\mathbf{i}, \mathbf{G}) d\tau = -\int \mathbf{K}_n d\sigma \quad (13-22)$$

and

$$-\int [\mathbf{r} \times \operatorname{div} \Theta(\mathbf{i}, \mathbf{G})] d\tau = -\int [\mathbf{r} \times \mathbf{K}_n] d\sigma \quad (13-23)$$

For the homogeneous superconductor in a stationary state we have, according to eq. 13-10, $\operatorname{div} T(\mathbf{H}) = -\operatorname{div} \Theta(\mathbf{i}, \mathbf{G})$. Therefore

$$\int \mathbf{F}_n d\sigma = \int \mathbf{K}_n d\sigma, \quad \int [\mathbf{r} \times \mathbf{F}_n] d\sigma = \int [\mathbf{r} \times \mathbf{K}_n] d\sigma \quad (13-24)$$

The net resultant force acting on an arbitrary superconductor can be calculated equally well either from the Maxwell stresses in the outside space or from the London stresses in the interior. The two methods give

⁵Because according to eqs. 13-8 and 13-1, $T_{a\beta}(\mathbf{H}) = -\mathbf{H}_a \mathbf{H}_{\beta} + \frac{1}{2} \delta_{a\beta} \mathbf{H}^2$.

⁶ \mathbf{r} is the vector whose components are the x_a .

the same results for the torque of the force only if the superconductor is of cubic crystal material. This always is true, although the separate forces \mathbf{F}_n and \mathbf{K}_n may have the same value, namely, $\mathbf{F}_n = \mathbf{K}_n = \frac{1}{2} \mathbf{H}^2 \mathbf{n}$, only for thick superconductors (compare eqs. 13-12, 13-19, and 7-37) and where no current is entering or leaving the superconductor.

However, when in Chap. 17 we calculate the work performed by the magnetic field during an arbitrary displacement of the phase boundary between normal and superconducting material, we have to start from the forces \mathbf{K}_n due to the London stresses, because they alone yield the actual force on every element of the surface.

(h) We still have to consider the term $\int (t_{32} - t_{23}) d\tau$ in eq. 13-17 as applied to the tensor $\Theta(\mathbf{i}, \mathbf{G})$. In the first place this equation, the other terms of which represent torques, shows that $t_{23} - t_{32}$ is the x component of a polar vector. We therefore introduce the vector θ with the components

$$\theta_1 = \Theta_{23} - \Theta_{32}, \quad \theta_2 = \Theta_{31} - \Theta_{13}, \quad \theta_3 = \Theta_{12} - \Theta_{21} \quad (13-25)$$

which according to eq. 13-2 we can also write vectorially as

$$\theta = [\mathbf{G} \times \mathbf{i}] \quad (13-26)$$

Equation 13-23 obviously has to be supplemented to read

$$-\int [\mathbf{r} \times \operatorname{div} \Theta(\mathbf{i}, \mathbf{G})] d\tau = -\int [\mathbf{r} \times \mathbf{K}_n] d\sigma + \int \theta d\tau \quad (13-27)$$

We can apply this equation not only to the whole volume of the superconductor but also to any part of it, provided only we keep in mind that in this case the forces \mathbf{K}_n are not effective, but are completely compensated by the London stresses from outside the region of integration. Equation 13-27 therefore states: The London stresses in a noncubic crystal superconductor produce a torque θ per unit volume. Because of the equality between action and reaction the material, in the stationary state, has to exert a torque $\theta' = -\theta$ on the superconduction mechanism. This result at first seems most surprising.

In classical mechanics there are already cases where a torque is necessary to maintain uniform motion. For example, a rigid body moving through liquid thrusts the latter to one side, in the absence of special symmetry conditions, and an impulse component perpendicular to the velocity \mathbf{v} is associated with the motion of the body. As this impulse is displaced along with the body, the angular momentum is changing by $[\mathbf{v} \times \mathbf{G}]$ per unit time, where \mathbf{G} represents the momentum of the body. If a torque of this direction and magnitude did not act on the body it would not be able to persist in its uniform motion. See Fig. 13-2.

Section (b) showed us that a momentum $\rho' \mathbf{G}$ per unit volume is associated with the supercurrent. The concept of a velocity \mathbf{v} of the super-



Fig. 13-2. The shaded area represents the vector product $[\mathbf{v} \times \mathbf{G}]$ i. e., the increase in angular momentum per unit time.

current is alien to the phenomenological theory. However, in so far as it has any meaning at all, it certainly has the value given by $\rho' \mathbf{v} = i\mathbf{r}$. Then the required torque per unit volume becomes

$$\theta' = [\mathbf{v} \times \rho' \mathbf{G}] = [i\mathbf{r} \times \mathbf{G}]$$

and this actually is equal to $-\theta$.

The combination of eqs. 13-27 and 13-10 gives for the whole superconductor

$$\int [\mathbf{r} \times \mathbf{F}_n] d\sigma = \int [\mathbf{r} \times \mathbf{K}_n] d\sigma + \int \theta' d\tau \quad (13-28)$$

instead of the second equation of 13-24.

The torque due to the Maxwell stresses in outside space, $\int [\mathbf{r} \times \mathbf{F}_n] \cdot d\sigma$ i. e., the moment of all the forces acting on the superconductor from outside, serves to increase the mechanical angular momentum of the superconductor (and any other bodies rigidly connected with it) by the amount $\int [\mathbf{r} \times \mathbf{K}_n] \cdot d\sigma$; and according to this equation angular momentum is also imparted to the superconducting mechanism.

(i) The results of this chapter concerning ponderomotive forces and the torque due to the field are so important for the further development of the theory that we wish to confirm them in the next chapter by expressing them in terms of an electrodynamic potential, at least for the stationary case. We derive this potential itself by a plausible generalization of the usual potential of the Maxwell theory.

CHAPTER 14

The Electrodynamic Potential

(a) We shall prove the following theorem with the unimportant restriction that only one superconductor is situated in the field, and the more important restriction that no ohmic current is supplied: In any quasi-stationary change of the field, occurring as a consequence of displacements of matter, the work ∂A performed by the field is equal to the decrease of the electrodynamic potential $-\partial V$ defined by

$$V = \frac{SI}{c} - \int_V \left\{ \frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) + \frac{1}{2} (i\mathbf{r} \cdot \mathbf{G}) \right\} d\tau \quad (14-1)^1$$

As in Chap. 12, I is the current flowing in the superconductor when the latter is in the form of a ring, S is the time invariant period of the superconduction potential Ψ ; if the superconductor is singly connected the

first term is absent. The integration has to be extended over the whole of space (as indicated by the suffix V). In the term $(\mathbf{M} \cdot \mathbf{H})$ the integration is taken only over the volume of the permanent magnets, in the term $\frac{1}{2} (i\mathbf{r} \cdot \mathbf{G})$ only over the volume of the superconductor: these two volumes are mutually exclusive, and the observation that no ferromagnetics ever become superconducting is therefore significant for the following proof. Electric field vectors do not appear because of our assumption that at every instant the state is infinitesimally near to a stationary state.

Let the material displacement be ∂u , a continuous vector function of position. The proof of the above theorem is effected as soon as we can express the decrease in potential in the form

$$-\partial V = \int_V \left\{ (\mathbf{K} \cdot \partial u) + \frac{1}{4} (\theta \cdot \text{curl } \partial u) \right\} d\tau \quad (14-2)$$

where \mathbf{K} means the force per unit volume determined by the well-known electrodynamic laws, and θ is the torque given by eq. 13-26. In other words we must show that the right-hand side of this expression is the work ∂A done by the field. The boundary conditions are that all material constants, including $\lambda_{\infty}\theta$ and μ do not change their values at any material point, furthermore that the ohmic current flows through any material surface with the same strength $\int i_n d\sigma'$ before and after the displacement, and also that the permanent magnetism $\int \mathbf{M}_n d\sigma'$ remains unchanged.² We shall therefore have

$$\partial \int i_n d\sigma' = 0, \quad \partial \int \mathbf{M}_n d\sigma' = 0 \quad (14-3)$$

We assume the condition of the constant ohmic current strength to be realized by arranging for suitable changes of the electromotive forces to compensate all changes of induction due to the displacements. We cannot introduce such a condition for the annular current in a superconductor. For this current it is the potential period S (Chap. 12) and not the current strength that remains unchanged, and for the current density here we have eq. 12-10,

$$c\mathbf{G} + \mathbf{A} = \text{grad } \Psi \quad (14-4)$$

(b) To formulate the assumptions under discussion mathematically we use at first some well-known equations. If $\delta\mu$ means the change of the parameter μ at a material point, $\partial\mu$, the change at a point fixed in space, the following relation holds:

$$\delta\mu = \partial\mu + (\partial u \cdot \text{grad } \mu)$$

As $\delta\mu$ shall be zero, we have to put

$$\partial\mu = -(\partial u \cdot \text{grad } \mu) \quad (14-5)$$

Furthermore, the change of flux of an arbitrary vector through a material surface integrates to

$$\delta \int \mathbf{K}_n d\sigma' = \int \{ \partial \mathbf{K} + \partial u \text{ div } \mathbf{K} - \text{curl } [\partial u \times \mathbf{K}] \} d\sigma'$$

² $d\sigma'$, in contrast to $d\sigma$, is a surface element participating in the displacement.

¹ Compare Von Laue reference ϵ and f in footnote 2, Chapter 3.

Therefore if we remember that here the stationary state means $\text{div } \mathbf{i}^0 = 0$, the conditions 14-3 yield

$$\partial \mathbf{i}^0 = \text{curl} [\partial \mathbf{u} \times \mathbf{i}^0] \quad (14-6)$$

$$\partial \mathbf{M} = -(\text{div } \mathbf{M}) \partial \mathbf{u} + \text{curl} [\partial \mathbf{u} \times \mathbf{M}] \quad (14-7)$$

Although the above considerations are based on well-known theorems⁸ we shall have to leave the proof of the next equation to the Appendix, namely that under the condition that the $\lambda_{\alpha\beta}$ do not change at any material point, the changes $\partial \lambda_{\alpha\beta}$ at a fixed point in space satisfy the equation

$$\frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta} = -\frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} (\partial \mathbf{u} \nabla \lambda_{\alpha\beta}) + \frac{1}{2} (\text{curl } \partial \mathbf{u} \cdot [\mathbf{G} \times \mathbf{i}^0]) \quad (14-8)$$

It is obvious that throughout the superconductor

$$\text{div } \mathbf{i}^0 = 0 \quad (14-9)$$

and at its boundary

$$\mathbf{i}_n = 0 \quad (14-10)$$

We take into account only one surface of discontinuity, namely the surface of the superconductor, and assume all other transitions to be continuous. In particular the permanent magnetization \mathbf{M} must go continuously to zero as we move from the interior of a permanent magnet; the actual conditions there can be taken care of afterwards by going to the limit.

(c) We proceed to the proof of eq. 14-2. According to eq. 14-1 we have

$$-\partial V = -\frac{S}{c} \partial I + \partial \int_V \left\{ \frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) + \frac{1}{2} (\mathbf{i}^0 \cdot \mathbf{G}) \right\} d\tau$$

The right-hand side can be split into six terms of the following type:

$$\begin{aligned} -\partial V &= \sum_{n=1}^5 \partial I_n - \frac{S}{c} \partial I \\ \partial I_1 &= \int_V (\mathbf{B} \cdot \partial \mathbf{H}) d\tau \\ \partial I_2 &= \int_P (\mathbf{H} \cdot \partial \mathbf{M}) d\tau \\ \partial I_3 &= \frac{1}{2} \int_V \mathbf{H}^2 \partial \mu d\tau \\ \partial I_4 &= \int_S (\mathbf{G} \cdot \partial \mathbf{i}^0) d\tau \end{aligned} \quad (14-11)^4$$

⁸ See for example, Margenau and Murphy, *Mathematics of Physics and Chemistry*, D. Van Nostrand, New York Chapter IV.

⁴ As before the suffixes s and P mean that the integration has to extend over the superconductor or the permanent magnets respectively.

$$\partial I_5 = \frac{1}{2} \int_S \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta} d\tau$$

This is because

$$\frac{1}{2} \partial (\mathbf{i}^0 \cdot \mathbf{G}) = \frac{1}{2} \partial \left(\sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \lambda_{\alpha\beta} \right) = \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \mathbf{i}_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_{\alpha} \mathbf{i}_{\beta} \partial \lambda_{\alpha\beta}$$

and

$$\frac{1}{2} \int_V \partial (\mathbf{i}^0 \cdot \mathbf{G}) d\tau = \partial I_4 + \partial I_5$$

We now use eq. 12-1, the theorem 5-1, and the fundamental equation II to rewrite ∂I_1 in the form

$$\partial I_1 = \int_V (\text{curl } \mathbf{A} \cdot \partial \mathbf{H}) d\tau = \int_V (\text{curl } \partial \mathbf{H} \cdot \mathbf{A}) d\tau = \frac{1}{c} \int_V [(\mathbf{A} \cdot \partial \mathbf{i}^0) + (\mathbf{A} \cdot \partial \mathbf{i}^0)] d\tau$$

Consequently by eq. 14-4,

$$\partial I_1 + \partial I_4 = \frac{1}{c} \int_V (\mathbf{A} \cdot \partial \mathbf{i}^0) d\tau + \int_S (\text{grad } \Psi \cdot \partial \mathbf{i}^0) d\tau$$

However, partial integration over the superconductor yields

$$\frac{1}{c} \int_S (\text{grad } \Psi \cdot \partial \mathbf{i}^0) d\tau = -\frac{1}{c} \int_S \Psi \text{div } \partial \mathbf{i}^0 d\tau - \frac{1}{c} \int_S \Psi \partial \mathbf{i}_n \cdot d\sigma$$

The first term vanishes because of eq. 14-9, and the surface makes no contribution because of eq. 14-10. But with a doubly connected body, a cut Q makes a contribution to the surface integral (compare eq. 12-17):

$$-\frac{1}{c} \int_Q \Psi \partial \mathbf{i}_n \cdot d\sigma = \frac{1}{c} (\Psi_2 - \Psi_1) \partial I = \frac{S}{c} \partial I$$

The sign is determined by the convention of Chap. 12 that a positive current flows through the cut in the direction $2 \rightarrow 1$. On the other hand, according to eqs. 14-6 and 12-1:

$$\begin{aligned} \frac{1}{c} \int_V (\mathbf{A} \cdot \partial \mathbf{i}^0) d\tau &= \frac{1}{c} \int_V (\mathbf{A} \cdot \text{curl} [\partial \mathbf{u} \times \mathbf{i}^0]) d\tau \\ &= \frac{1}{c} \int_V (\mathbf{B} \cdot [\partial \mathbf{u} \times \mathbf{i}^0]) d\tau = \frac{1}{c} \int_V (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{B}]) d\tau \end{aligned}$$

Consequently we have

$$\partial I_1 + \partial I_4 = \frac{S}{c} \partial I + \int_V (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{B}]) d\tau \quad (14-12)$$

Again, using eqs. 13-26 and 14-8 we can rewrite

$$\partial I_s = \frac{1}{2} \int_V \left[- \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla \lambda_{\alpha\beta} + (\theta \cdot \text{curl } \partial \mathbf{u}) \right] d\tau \quad (14-13)$$

Furthermore, by eq. 14-7, the theorem 5-1, and the fundamental equation III (remembering that the supercurrent \mathbf{j} is absent from the interior of the permanent magnets) we get

$$\begin{aligned} \partial I_s &= \int_V \left\{ \mathbf{H} \cdot (\text{curl } [\partial \mathbf{u} \times \mathbf{M}] - \partial \mathbf{u} \text{ div } \mathbf{M}) \right\} d\tau \\ &= \int_V \left\{ \frac{1}{c} ([\partial \mathbf{u} \times \mathbf{M}] \cdot \mathbf{i}^0) - (\partial \mathbf{u} \cdot \mathbf{H} \text{ div } \mathbf{M}) \right\} d\tau \\ &= \int_V \left\{ - \frac{1}{c} (\partial \mathbf{u} \times \mathbf{M}) \cdot [\mathbf{i}^0 \times \mathbf{M}] - (\partial \mathbf{u} \cdot \mathbf{H} \text{ div } \mathbf{M}) \right\} d\tau \end{aligned} \quad (14-14)$$

Finally it follows from eq. 14-5 that

$$\partial I_s = - \frac{1}{2} \int_V \mathbf{H}^2 (\partial \mathbf{u} \cdot \text{grad } \mu) d\tau \quad (14-15)$$

By adding together eqs. 14-12 to 14-15 and using eq. 14-11 we obtain

$$- \partial V = \int_V \left\{ (\mathbf{K} \cdot \partial \mathbf{u}) + \frac{1}{2} (\theta \cdot \text{curl } \partial \mathbf{u}) \right\} d\tau \quad (14-16)$$

with the value of the vector \mathbf{K} given by

$$\mathbf{K} = \frac{1}{c} [\mathbf{i}^0 \times \mu \mathbf{H}] - \mathbf{H} \text{ div } \mathbf{M} - \frac{1}{2} \mathbf{H}^2 \text{ grad } \mu - \frac{1}{2} \sum_{\alpha\beta} \mathbf{i}_\alpha \mathbf{i}_\beta \nabla \lambda_{\alpha\beta} \quad (14-17)$$

This is the most general expression for the force exerted by a stationary magnetic field on a unit volume of matter. The first term represents the effect of the field on ohmic current, the second term is the effect on the density of permanent magnetic charges as measured by $-\text{div } \mathbf{M}$, the third is the equally familiar force on regions of magnetic inhomogeneity, the fourth is the force on an inhomogeneous superconductor appearing in eq. 13-10. Equations 14-16 and 14-17 contain therefore the proof of the earlier statement that $\mathbf{K} = 0$ for the homogeneous superconductor, for then, by eq. 13-10 $\mathbf{K} = 0$.

(d) The theorem $\partial A = -\partial V$ comes from the Maxwell theory, and our definition 14-1 is simply a plausible extension of the definition of that theory. That we have arrived at exactly the same conclusions about the force \mathbf{K} and the torque θ by a line of reasoning that avoids the stress concept used in Chap. 13 on the argument about the London stresses seems to us to be a valuable confirmation of the essential truth of that theory. In addition, the observation that ferromagnetics are unable to show super-

conductivity appears in a new light. Otherwise we would have found in eq. 14-14 another term

$$- \frac{1}{c} (\partial \mathbf{u} \cdot [\mathbf{i}^0 \times \mathbf{M}])$$

also entering the expression for the force \mathbf{K} , and this would have been in conflict with the fact that the existence of persistent currents demands that \mathbf{K} be zero in a homogeneous superconductor. It seems as though permanent magnetism and superconductivity are mutually exclusive not only in the temperature ranges that happen to have been observed to date, but also fundamentally so.

(e) According to eq. 12-21 the total (available) energy of the field is

$$U = \frac{1}{2} \int_V \{ \mu \mathbf{H}^2 + (\mathbf{i} \cdot \mathbf{G}) \} d\tau = \frac{1}{2c} \left\{ S I + \int_V (\mathbf{A} \cdot \mathbf{i}^0) d\tau \right\} - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (14-18)$$

and so according to eq. 14-1,

$$V = \frac{1}{2c} \left[S I - \int_V (\mathbf{A} \cdot \mathbf{i}^0) d\tau \right] - \frac{1}{2} \int_V (\mathbf{H} \cdot \mathbf{M}) d\tau \quad (14-19)$$

If the field is produced only by an annular current I and permanent magnets, then $V = U$ and the work $\partial A = -\partial U$. Conversely if the field is produced by ohmic currents, $V = -U$ and $\partial A = \partial U$. The amount of work $2 \partial A$ has then to be performed by the electromotive forces keeping the currents constant. This second point differs from the corresponding theorem of the Maxwell theory in that here superconductors (but with no annular currents) are permitted to be in the field.

Eliminating the term $S I/c$ from eq. 14-1 by means of eq. 12-19 we get a new expression for V of which we shall make immediate use, namely,

$$V = \frac{1}{c} \int_V (\mathbf{A} \cdot \mathbf{i}) d\tau + \frac{1}{2} \int_V (\mathbf{i} \cdot \mathbf{G}) d\tau - \int_V \left[\frac{1}{2} \mu \mathbf{H}^2 + (\mathbf{M} \cdot \mathbf{H}) \right] d\tau \quad (14-20)$$

(f) With the help of the potential V we shall now confirm the theorem of Chap. 13 (c) that the surface of the superconductor experiences an inward pull $\frac{1}{2} (\mathbf{i} \cdot \mathbf{G})$ at all points where there is no current entering or leaving. For this purpose we ignore all displacements of matter, but displace the boundary between a superconducting and a chemically identical normal conducting phase in such a way that every surface element $d\sigma$ suffers a displacement $\partial \mathbf{u}$ normal to $d\sigma$. We take $\partial \mathbf{u}$ to be positive if $d\sigma$ moves toward the interior of the superconductor. If before the displacement the superconducting phase occupied the region s , afterwards it occupies the smaller region s' . A finite change therefore takes place in the layer $s - s'$; supercurrent and supermomentum suddenly drop to zero. But as this layer is infinitely thin, the effects of this change at all other points in space is infinitesimal. In general μ and $\lambda_{\alpha\beta}$ do not change at all, and the same is true of the current density \mathbf{i}^0 , as we shall again keep the ohmic currents constant.

Starting from eq. 14-20 we split the change $-\partial V$ into five parts:

$$\begin{aligned}
 -\partial V &= \sum_{k=1}^5 \partial I_k \\
 \partial I_3 &= \int_V (\mathbf{B} \cdot \partial \mathbf{H}) d\tau \\
 \partial I_1 &= -\frac{1}{c} \int_V \partial (\mathbf{A} \cdot \mathbf{i}^s) d\tau \\
 \partial I_4 &= \int_{s_1-s'} (\mathbf{A} \cdot \mathbf{i}^s) d\tau \\
 \partial I_5 &= -\frac{1}{2} \int_{s_1-s'} (\mathbf{i}^s \cdot \mathbf{G}) d\tau
 \end{aligned} \quad (14-21)$$

The transformation proceeds as follows.

First, by eq. 14-4 we have

$$\partial I_1 + \partial I_2 = -\frac{1}{c} \int_V [(\text{grad } \Psi \cdot \partial \mathbf{i}^s + (\mathbf{i}^s \cdot \partial \mathbf{A}))] d\tau$$

Then in spite of the infinitesimal $\partial \mathbf{H}$ in the layer $s-s'$ by which the superconductor is reduced, $\text{curl } \partial \mathbf{H} = -\mathbf{i}^s/c$ is finite, but $\partial \mathbf{i}^0 = 0$ everywhere; remembering this and using eq. 12-1 and the theorem 5-1 it follows that

$$\partial I_3 = \frac{1}{c} \left[\int_V (\mathbf{A} \cdot \partial \mathbf{i}^s) d\tau - \int_{s-s'} (\mathbf{A} \cdot \mathbf{i}^s) d\tau \right]$$

Adding up ∂I_1 to ∂I_4 the contributions of the layer $s-s'$ cancel. Again recalling eq. 14-4 there remains

$$\begin{aligned}
 \sum_{k=1}^4 \partial I_k &= \frac{1}{c} \int_V [(\mathbf{A} - \text{grad } \Psi) \cdot \partial \mathbf{i}^s] - (\mathbf{i}^s \cdot \partial \mathbf{A})] d\tau \\
 &= -\int_V \left\{ (\mathbf{G} \cdot \partial \mathbf{i}^s) + \frac{1}{c} (\mathbf{i}^s \cdot \partial \mathbf{A}) \right\} d\tau
 \end{aligned}$$

Now because of the symmetry of the tensor $\lambda_{\alpha\beta}$, which enters once more as an important condition, we have

$$(\mathbf{G} \cdot \partial \mathbf{i}^s) = \sum_{\alpha\beta} \lambda_{\alpha\beta} \mathbf{i}_\alpha^s \partial \mathbf{i}_\beta^s = \sum_{\alpha\beta} \lambda_{\alpha\beta} \partial \mathbf{i}_\alpha^s \mathbf{i}_\beta^s = (\mathbf{i}^s \cdot \partial \mathbf{G})$$

and so from eqs. 14-4 and 14-9 and the constancy of $S = \Psi_2 - \Psi_1$ we have

$$\begin{aligned}
 \sum_{k=1}^4 \partial I_k &= -\int_V \left\{ \mathbf{i}^s \cdot \partial \left[\mathbf{G} + \frac{\mathbf{A}}{c} \right] \right\} d\tau = -\frac{1}{c} \int_V (\mathbf{i}^s \cdot \text{grad } \partial \Psi) d\tau \\
 &= \frac{1}{c} \int_V \Psi \text{div } \mathbf{i}^s d\tau - I (\Psi_2 - \Psi_1) = 0
 \end{aligned} \quad (14-22)$$

There remains only the term ∂I_5 in eq. 14-21 to be considered. In the layer $s-s'$ however, putting the volume element $d\tau = d\sigma' \cdot d\mathbf{u}$ we get by surface integration

$$\partial A = -\partial V = \frac{1}{2} \int_V (\mathbf{i}^s \cdot \mathbf{G}) \partial \mathbf{u} \cdot d\sigma' \quad (14-23)$$

From this we deduce that $\frac{1}{2} (\mathbf{i}^s \cdot \mathbf{G})$ is in fact the pull acting over the element $d\sigma'$ toward the interior of the superconductor.

(g) From the section (f) we can also make the following deduction. Given the relative positions of all bodies, the ohmic currents in them, the permanent magnetism, and the potential "period" S of all possible annular currents which may eventually appear, the stationary field adjusts itself to minimize the electrodynamic potential.

If we disregard the displacements $\partial \mathbf{u}$, the integrals ∂I_4 and ∂I_5 in eq. 14-21 vanish for every virtual displacement of the field. Then eq. 14-22 gives

$$-\partial V = \sum_{k=1}^3 \partial I_k = 0$$

If there is no ohmic current contributing to the field, then $V = U$ according to section (e). The field adjusts itself to minimize the free energy. Also a persistent current by itself corresponds to a minimum of the free energy, of course with the boundary condition that the potential "period" S be given. Without such a condition the law of the minimum free energy cannot be proved.

CHAPTER 15

Electric Waves in Superconductors with Cubic Crystal Structure

(a) According to the fundamental equation IX changes in time always produce an electric intensity \mathbf{E} in a superconductor; this in turn produces an ohmic current density \mathbf{i}^0 in addition to the supercurrent, and also Joule heat according to the energy equation 5-5. This is the fundamental difference from static fields. To describe periodic waves, in what follows we always use complex expressions for the field strengths and all quantities linearly related to them. The waves will be designated by their angular frequency ω , the numerical frequency ν being $\omega/2\pi$. All the complex expressions are taken proportional to $e^{i\omega t}$.

It follows from VII a and IX for cubic crystal superconductors that

$$\mathbf{i}^0 = \sigma \mathbf{E} = \omega \sigma \lambda \mathbf{i}^s e^{i\omega t} \quad (15-1)$$

The supercurrent i^s is therefore lagging in phase by a quarter period behind the ohmic current and the field strength E . For the ratio of the amplitudes of the two waves we have

$$\frac{|i^s|}{|i^o|} = \omega \sigma \lambda \quad (15-2)$$

The greater ω the greater the influence of i^o compared with i^s . The pure number $\omega \sigma \lambda$ which we encounter here for the first time, will play a fundamental role in the ensuing calculations. The total current density is connected with the field strength by the relation

$$i = i^o + i^s = E \frac{\omega \sigma \lambda - i}{\omega \lambda}$$

$$= E \frac{1 + i \omega \sigma \lambda}{i \omega \lambda} \quad (15-3)$$

(b) Because of the inevitable production of Joule heat a progressive wave in a superconductor is damped just as in a normal conductor. For a plane polarized wave progressing in the z direction we write

$$E_x = E_0 \exp i \omega \left\{ t - \frac{(n - i\kappa)z}{c} \right\}, \quad E_y = E_z = 0 \quad (15-4)$$

This satisfies the condition $\text{div } E = 0$. According to the fundamental relation I it follows from this that

$$H_x = 0, \quad H_y = (n - i\kappa) E \exp i \omega \left\{ t - \frac{(n - i\kappa)z}{c} \right\}, \quad H_z = 0 \quad (15-5)$$

Consequently for waves in a superconductor the electric field strength, magnetic field strength, and direction of propagation are perpendicular to each other and form in this order a right-handed system, as is otherwise known to be the case. However, unlike the behavior of waves in a non-conductor, E and H do not oscillate in phase, E in general lagging in phase behind H . The amplitude decreases with increasing z by the factor $e^{-\omega \kappa z/c}$, the energy density by $e^{-2\omega \kappa z/c}$. κ is called the extinction coefficient, n the refractive index. Both are pure numbers and functions of ω .

Inserting the value of E from eq. 15-4 in the telegrapher's equation $W(E) = 0$ (compare Chap. 6: it is equally possible to insert the value of H from eq. 15-5 in $W(H) = 0$), because

$$W(E) = \Delta E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial E}{\partial t} - \frac{E}{\lambda^2 c^2}$$

one obtains the relation

$$(n - i\kappa)^2 = \frac{(\omega^2 \lambda - 1 - i \omega \sigma \lambda)}{\omega^2 \lambda} \quad (15-6)$$

The two real numbers n and κ are determined by

$$n^2 = \frac{1}{2} \frac{[(\omega^2 \lambda - 1) + \sqrt{(\omega^2 \lambda - 1)^2 + (\omega \sigma \lambda)^2}]}{\lambda \omega^2} \quad (15-7)$$

$$\kappa^2 = \frac{1}{2} \frac{[-(\omega^2 \lambda - 1) + \sqrt{(\omega^2 \lambda - 1)^2 + (\omega \sigma \lambda)^2}]}{\lambda \omega^2}$$

If $\omega^2 \lambda < 1$, then $n < \kappa$ and the wavelength $2\pi c/\omega n$ is greater than the logarithmic damping factor, i. e., the distance in which the amplitude decreases by a factor $e^{-2\pi}$ or 0.2%. No wave can actually develop at all under such circumstances. The field is quasistatic and its distribution in space is similar to a static one. If indeed $\omega^2 \lambda$ and $\omega \sigma \lambda$ are small numbers, the following approximations hold:

$$n = \frac{1}{2} \sigma \lambda^{\frac{1}{2}}, \quad \kappa = \frac{1}{\omega \lambda^{\frac{1}{2}}} \gg n \quad (15-8)$$

This can be seen in the simplest way by forming $n^2 - \kappa^2$ and $2n\kappa$ from eq. 15-8, and comparing with eq. 15-6. Since in this case $\omega \kappa/c = \beta$, the amplitude decreases by the factor $e^{-\beta z}$ just as in the static case.

On the other hand if $\omega^2 \lambda > 1$, then $n > \kappa$ according to eq. 15-7, and the wavelength is therefore smaller than the logarithmic damping factor, so a whole series of waves is produced with only gradually decreasing amplitude. If indeed $\omega^2 \lambda \gg 1$, then the unity in the numerator of eq. 15-6 is negligible and we obtain the approximate values

$$n = 1 + \frac{(\sigma/\omega)^2}{8}, \quad \kappa = \frac{\sigma}{2\omega} \quad (15-9)$$

which no longer depend on the superconductivity constant λ .

But such a condition can only be realized immediately below the transition temperature where λ is comparatively large. As soon as λ attains values of the order 10^{-31} sec^2 at somewhat lower temperatures, this condition is hardly possible any longer because, just as with the Maxwell theory, our theory cannot be regarded as valid for arbitrarily high frequencies. Let us consider the situation with mercury for which direct determinations of β , and therefore also of λ , are available (see Chap. 1 and 12). Its conductivity σ at room temperatures is about 10^{17} sec^{-1} in Lorentz units (4π times its value in esu); it is about 500 times greater just above the transition temperature: 10^{13} sec^{-1} . Therefore for $\omega = 10^{10}$ per sec, $\omega^2 \lambda = 10^{-11}$, and $\omega \sigma \lambda = 10^{-2}$ (short Hertzian waves, high radio frequency), and for $\omega = 10^{14}$ per sec, $\omega^2 \lambda = 10^{-3}$ and $\omega \sigma \lambda = 10^2$ (infrared waves).

In the first case the ohmic current is about one hundred times smaller than the supercurrent; in the second case about one hundred times greater, according to eq. 15-2. In the first case the unity is the dominating term in the numerator of eq. 15-6; in the second case the number $i \omega \sigma \lambda$, so that, just as for a normal conductor,

$$n - i\kappa = (1 - i) \sqrt{\frac{\sigma}{2\omega}} \quad (15-10)$$

This indicates a complete identity between normal and superconductors for all optical processes. If only the supercurrent were to exist in the superconductor, then the superconductor would be transparent. The fact that there is no visible difference between the normal and the superconductor [Chap. 1 (d)] is a decisive proof of the existence of the ohmic current.

For $\omega = 10^{14}$ per sec and $\sigma = 10^{19}$ per sec, eq. 15-10 gives n and κ the order of magnitude between 10^2 and 10^3 .

(c) If $\omega = 10^{10}$ per sec then according to the above figures the conditions for the validity of eq. 15-8 are satisfied. The refractive index n then has the order of magnitude 10^3 and the extinction coefficient 10^6 for radio frequency waves. The reflectivity of a specimen for a wave incident perpendicularly from empty space can be calculated from the well-known optical expression

$$\frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} = 1 + \left(\frac{n-1}{\kappa} \right)^2 = 1 - \frac{4n}{\kappa} = 1 - 2\omega^2 \sigma \lambda'^2. \quad (15-11)^1$$

Under the present conditions this expression can be simplified to read

$$1 + \left(\frac{n-1}{\kappa} \right)^2 = 1 - \frac{4n}{\kappa} = 1 - 2\omega^2 \sigma \lambda'^2. \quad (15-11)^1$$

Consequently that fraction of the energy given by the second term is absorbed in the superconductor and amounts, according to the figures used above, to about 10^{-8} .

CHAPTER 16

The High-Frequency Resistance of Superconductors

(a) A direct current is distributed uniformly over the cross section of a normally conducting cylinder. Alternating current, however, is confined to a thin layer at the surface which becomes thinner with increasing frequency. The induction from the magnetic field of the alternating current itself protects the interior from the current. This is the "skin effect" that exists in conductors of any form. In the superconductor a tendency to the same effect already exists even with the direct current because of the coupling between the supercurrent and the magnetic field expressed by eq. X. For high frequency alternating current this Meissner effect and the skin effect reinforce each other. The penetration depth of the field of such an alternating current is then smaller than for direct current in the super-

¹ See the discussion of eq. 16-18 for the meaning of the number $\omega^2 \sigma \lambda'^2$.

conductor and smaller than for alternating current of the same frequency in a normal conductor. The skin effect eventually causes a very substantial decrease in the cross section that actually carries the current in a normal conductor and thus may cause a considerable increase of the resistance. A changing field, according to Chaps. 7 and 15, produces an average resistance in a superconductor. This resistance increases with increasing frequency not only because of the decrease of the conducting cross section, but also because of the increasing transfer of current from the supercurrent to the ohmic current in accordance with eq. 15-2. We shall describe this increase quantitatively for the cubic crystal material.

(b) First we have to determine the current density as a function of position. The telegrapher's equation of Chap. 6 for the total current density reads:

$$W(i) \equiv \Delta i - \frac{1}{c^2} \frac{\partial^2 i}{\partial t^2} - \frac{\sigma}{c^2} \frac{\partial i}{\partial t} - \frac{i}{\lambda c^2} = 0$$

For periodic processes this becomes

$$\Delta i - i \frac{(\omega^2 + i\omega\sigma + \lambda^{-1})}{c^2} = 0$$

As we are confining ourselves to frequencies less than 10^{10} per sec, the first term in the brackets is small compared with the second term when $\sigma = 10^{19}$ per sec (see Chap. 15). We therefore neglect this term and write $\Delta i - k^2 i = 0$

for superconductors where

$$k = \frac{(1 + i\omega\sigma\lambda)^{1/2}}{c\sqrt{\lambda}} \quad (16-1)^1$$

As the neglected term arises from the term $\partial E / \partial t$ in the fundamental equation II, it means we are neglecting the displacement current as compared with the conduction current. We complete the definition of k by choosing both its roots to be positive, i. e., both the real and the imaginary part of k shall be positive.

Going to the limit $\lambda \rightarrow \infty$ leads to the normal conductor, because in this limit the last term of $W(i)$ vanishes and instead of eq. 16-1 we have the differential equation

$$\Delta i - k_n^2 i = 0, \quad k_n = \frac{\sqrt{i\omega\sigma}}{c} \quad (\text{normal conductor}) \quad (16-2)$$

In both cases the boundary conditions are: $\text{div } i = 0$, i is finite and continuous throughout the interior; and, because we are discussing quasi-stationary currents, $i_n = 0$ at all surfaces; and finally integration of i

¹ The following relation exists between k and the refractive index and extinction coefficient:

$$k = i\omega \frac{(n - i\kappa)}{c}$$

over any cross section yields the total current strength $I e^{\omega t}$. We treat \mathbf{I} as a real quantity.

We obtain the magnetic field from the current density by the fundamental equation II, which, neglecting the displacement current, reads:

$$\text{curl } \mathbf{H} = \frac{1}{c} \quad (16-3)$$

In the external space we have the additional requirement that \mathbf{H} is the negative gradient of a potential obeying the equation $\Delta \varphi = 0$. Besides requiring that \mathbf{H} be divergence free, the boundary conditions require also that \mathbf{H} be finite and continuous at the surface of the conductor, and vanish sufficiently rapidly at infinity. The calculations are carried out in the same way for both the superconductor and the normal conductor except that in the first case one has to use the \mathbf{k} of eq. 16-1 and in the other the \mathbf{k}_n of eq. 16-2.

We can also derive the electric field from the current density. For the normal conductor we use the fundamental equation VII a,

$$\mathbf{E} = \frac{1}{\sigma} \quad (\text{normal conductor})$$

while for the superconductor we use eq. 15-3,

$$\mathbf{E} = \frac{i\omega\lambda i}{(1 + i\omega\sigma\lambda)} \quad (\text{superconductor})$$

We can therefore derive the field strength for the superconductor from that of the normal conductor by multiplying the latter by the factor

$$\frac{i\omega\sigma\lambda}{(1 + i\omega\sigma\lambda)} \quad (16-4)$$

The last step consists of determining the Poynting energy current vector $c[\mathbf{E} \times \mathbf{H}]$. The divergence of the time average of this vector gives the Joule heat per unit volume and unit time, and the integral $c \int [\mathbf{E} \times \mathbf{H}] \cdot d\sigma$ is therefore the Joule heat developed in the enclosed volume per unit time. From the complex solutions for \mathbf{E} and \mathbf{H} obtained in the manner just described, we calculate the time average of the Joule heat as the real part of $\frac{1}{2} c [\mathbf{E} \times \mathbf{H}^*]$,² where \mathbf{H}^* is the complex conjugate to \mathbf{H} .

²If one has the complex representations for two field quantities A and B :

$$A = A_0 e^{i\omega t} = |A_0| e^{i(\omega t - \varphi)}, \quad B = B_0 e^{i\omega t} = |B_0| e^{i(\omega t - \psi)}$$

they each represent two real quantities, one pair of which is

$$A = |A_0| \cos(\omega t - \varphi), \quad B = |B_0| \cos(\omega t - \psi)$$

The time average of the product of the two quantities is then

$$\frac{1}{2} |A_0| |B_0| \cos(\varphi - \psi)$$

This result can be obtained most simply from the complex representation as

$$\frac{1}{2} \text{Real Part of } (A B^*)$$

Having calculated $\frac{1}{2} c [\mathbf{E} \times \mathbf{H}^*]$ for the normal conductor, we obtain its value for the superconductor by substituting \mathbf{k} for \mathbf{k}_n and multiplying by the factor 16-4. From the real part of this we derive the Joule heat Q and the resistance

$$R = \frac{Q}{I^2} \quad (16-5)$$

As the factor 16-4 becomes unity, and $\mathbf{k} \rightarrow \mathbf{k}_n$ when λ approaches infinity, the resistance of the superconductor goes over continuously into that of the normal conductor at the transition temperature provided that the conductivity σ is not discontinuous there.

The simplest solutions of the differential equations 16-1 and 16-2, corresponding to the plane waves already discussed in Chap. 15, are

$$\mathbf{H} = \mathbf{H}_0 e^{-kz} \quad \text{or} \quad \mathbf{H} = \mathbf{H}_0 e^{-k_n z}$$

Evidently the real part of \mathbf{k} , or of \mathbf{k}_n , respectively, determines the decrease of amplitude with increasing z . Separating the real and imaginary parts of \mathbf{k} and \mathbf{k}_n ,

$$\mathbf{k} = \frac{1}{c \sqrt{2\lambda}} \{ [1 + \sqrt{1 + (\omega\sigma\lambda)^2}]^{1/2} + i [-1 + \sqrt{1 + (\omega\sigma\lambda)^2}]^{1/2} \} \quad (16-6)$$

$$\mathbf{k}_n = \sqrt{\frac{1}{2} \omega \sigma \frac{(1+i)}{c}} \quad (16-7)$$

The real part of \mathbf{k} is thus greater than that of \mathbf{k}_n , or waves in the superconductor decay more rapidly toward the interior than they do in the normal conductor, other things being equal, as already observed in section (a).

(c) Using the method described above we calculate the a-c resistance of a circular cylinder of radius R carrying a current $I e^{\omega t}$, first for a normal conductor. We use the same cylindrical coordinates as in Chap. 8. As the differential equation 16-2 differs from $\Delta u - \beta^2 u = 0$ only in the notation used for the constants, we can take over eq. 8-9 for the current by replacing β by \mathbf{k}_n and \mathbf{I} by $I e^{\omega t}$.

$$I_r = 0, \quad I_\theta = 0, \quad I_z = \frac{i k_n I}{2\pi R} e^{\omega t} \frac{I_0(i k_n r)}{I_1(i k_n R)} \quad (16-8)$$

Taking over eq. 8-11 in the same way satisfies eq. 16-3:

$$\mathbf{H}_r = 0, \quad \mathbf{H}_\theta = \frac{I}{2\pi c R} e^{\omega t} \frac{I_1(i k_n r)}{I_1(i k_n R)}, \quad \mathbf{H}_z = 0 \quad (16-9)$$

For thin cylinders ($k_n R \ll 1$) to a first approximation $I_0(x) = 1$ and $I_1(x) = \frac{1}{2} x$; compare the series 8-6. We therefore conclude, as in Chap. 8, that the current is uniformly distributed over the cross section in this case. For thick cylinders ($k_n R \gg 1$) we have approximately:

$$\begin{aligned} I_0(i k_n r) &= (2\pi i k_n r)^{-1/2} \left(1 + \frac{1}{8 k_n r} \right) \exp \left(k_n r + \frac{1}{4} \pi i \right) \\ I_1(i k_n r) &= (2\pi i k_n r)^{-1/2} \left(1 - \frac{1}{8 k_n r} \right) \exp \left(k_n r + \frac{3}{4} \pi i \right) \end{aligned} \quad (16-10)^3$$

³It is essential here that the real part of k_n be positive.

It follows that I and H decay exponentially with decreasing r . There is a protective layer of thickness $(\text{Re } k_n)^{-1}$ in this case and the skin effect is pronounced.

The Poynting energy flow vector has only one component, an r component with magnitude $c E_r H_\theta = -(c/\sigma) I_r H_\theta$. The mean rate at which energy enters unit length of the cylinder is therefore

$$Q = 2\pi R \frac{c}{2\sigma} \text{Re}(I_r H_\theta^*)_{r=R} \quad (16-11)$$

Let Z be defined in such a way that

$$Q = I^2 \text{Re}(Z) \quad (16-12)$$

so that by eq. 16-5 the resistance per unit length is

$$W = \text{Re}(Z) \quad (16-13)$$

However, from eqs. 16-8 and 16-9

$$Z = \frac{1}{\sigma \pi R^2} \left(\frac{1}{2} I_n R \right) \frac{I_0(I_n R)}{I_1(I_n R)} \quad (\text{normal conductor}) \quad (16-14)$$

The first fraction is the d-c resistance of the normal conductor. For thin cylinders the other fractions reduce to unity according to eq. 8-6.

This well-known result for the a-c resistance of the normal conductor holds for the superconductor if we write k instead of k_n and multiply with the factor 16-4. The resistance then becomes the real part of

$$Z = \frac{1}{\sigma \pi R^2} \left[\frac{i\omega\sigma\lambda}{(1+i\omega\sigma\lambda)} \right] \left(\frac{1}{2} I_n R \right) \frac{I_0(I_n R)}{I_1(I_n R)} \quad (\text{superconductor}) \quad (16-15)$$

(d) We limit the discussion of this equation to the case of a thick cylinder, $(|k|R \gg 1)$. From eq. 16-10 it follows for this case that

$$\frac{I_0(I_n R)}{I_1(I_n R)} = -i \left(1 + \frac{1}{2kR} \right) \quad (16-16)$$

Noticing eq. 16-1 we see that this reduces eq. 16-14 to

$$Z = \frac{1}{2\pi c R} \left(\frac{i\omega\sqrt{\lambda}}{1+i\omega\sigma\lambda} \right) \left[1 + \frac{1}{2} \frac{1}{c\sqrt{\lambda}} \frac{(1+i\omega\sigma\lambda)^{-1/2}}{R} \right] \quad (16-17)$$

Assume at first that $\omega\sigma\lambda \ll 1$, which is surely justified when $\omega \leq 10^{10}$ per sec and $\lambda = 10^{-31}$ sec² (see Chap. 15). Developing the denominator of eq. 16-16 in series we then find

$$Z = \frac{\omega^2\sigma\lambda^{3/2}}{4\pi c R} + \frac{\omega^2\sigma\lambda^2}{4\pi R^2} + i \left(\frac{\omega\lambda^{1/2}}{2\pi c R} + \frac{\omega\lambda}{4\pi R^2} \right) \quad (16-18)$$

Consider the real part of eq. 16-17, the resistance W . Its value is

$$W = \frac{\omega^2\sigma\lambda^{3/2}}{4\pi c R} = \frac{(\omega\sigma\lambda)^2}{4\pi\sigma c R \sqrt{\lambda}} \quad (16-19)$$

except for an additional term only $c/\sqrt{\lambda} \div R$ compared with the first term $(c/\sqrt{\lambda})$ is the penetration depth).

The resistance turns out to be proportional to $(\omega\sigma\lambda)^2$ because the number $\omega\sigma\lambda$ is a measure of the extent to which the ohmic current i^0 participates in the transport of electricity, whereas the Joule heat is proportional to the square of i^0 . In the denominator of eq. 16-18 there is the product of the cylinder's circumference, $2\pi R$, and the penetration depth $c/\sqrt{\lambda}$, and this is an approximate measure of the area that carries the current. Multiplying this is the conductivity σ , because it is this product of cross-sectional area and conductivity that matters. We may take $c/\sqrt{\lambda}$ rather than the reciprocal of the real part of k to be the penetration depth because the supercurrent far outweighs the ohmic current in the present approximation.

Equation 16-18 can be used for all temperatures that are at least some tenths of a degree below the transition temperature, for λ then has the assumed order of magnitude, 10^{-31} sec². With increasing temperature λ increases and so does the resistance. However, some tenths of a degree below the transition temperature, λ becomes so great that the equation fails.

To discuss the temperature dependency of the resistance in general we introduce the auxiliary quantity θ defined by

$$\omega\sigma\lambda = \tan\theta \quad 0 < \theta \leq \frac{1}{2}\pi \quad (16-20)$$

Neglecting the small second term inside the bracket in eq. 16-16 we get the transformation

$$2\pi c R Z = i\omega\sqrt{\lambda} \cos\theta e^{-\frac{1}{2}i\theta}$$

The real part of this is therefore

$$2\pi c R W = \int \frac{\omega}{\sigma} \sqrt{\omega\sigma\lambda} \cos\theta \sin\frac{1}{2}\theta = \int \frac{\omega}{\sigma} \sqrt{\sin\theta} \sin\frac{1}{2}\theta$$

At the transition temperature $\lambda = \infty$ and therefore $\theta = \frac{1}{2}\pi$. As the conductivity has perhaps a different value σ_c at the transition temperature than at lower temperatures, we have to put

$$2\pi c R W_c = \int \frac{\omega}{2\sigma_c} \quad (16-21)$$

Dividing eq. 16-20 into the previous equation yields

$$\int \frac{\sigma}{\sigma_c} \frac{W}{W_c} = \sqrt{2} \sin\theta \sin\frac{1}{2}\theta \quad (16-22)$$

From the way it was derived, eq. 16-20 evidently gives the resistance of a normal conductor having conductivity σ_c , assuming a pronounced skin effect: $\text{Re}(k_n R) \gg 1$. This is easily confirmed from eqs. 16-3 and 16-15. Therefore eq. 16-21 again shows that there is a continuous transition from the high-frequency resistance of the normal conductor to that of the superconductor.

(e) All quantities depending on the geometry of the superconductor have disappeared from eq. 16-21, and in fact this equation holds for other forms than the straight circular cylinder.

To see this let us consider a normal conductor having some elongated form to the ends of which the current leads are attached, at a distance L apart. It could, for example, be a wire wound in the form of a coil. Its d-c resistance would be $L/\sigma A$, where A is the mean cross section. However for alternating current with pronounced skin effect, the current does not fill the whole cross section, but only a thin superficial layer the thickness of which is given by $(\text{Re } k_n)^{-1}$. Let the cross section of this surface layer have a mean linear dimension S normal to its thickness. Then the resistance becomes $W = L(\text{Re } k_n)/\sigma S$.

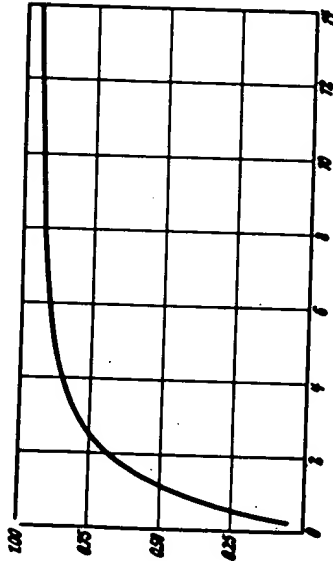


Fig. 16-1. Curve of $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$ against $\tan \theta$.

As the example of the cylinder shows, the calculation leads initially to a complex quantity Z the real part of which is the resistance W . The equation for Z can be nothing else than $Z = L k_n / \sigma S$ because the real and imaginary parts of k_n do not appear explicitly. In fact the eq. 16-13 does have this form if we remember that it refers to $L = 1$, and if, in accordance with eq. 16-15 we put the ratio of the Bessel functions equal to $-i$. Going over to the superconductor, which requires the replacement of k_n by k and the multiplication by the factor 16-4 we obtain

$$Z = \frac{L k}{S \sigma (1 + i \omega \sigma \lambda)}$$

By again applying eq. 16-15 we confirm that the factor (L/S) equals the factor $(1/2\pi R)$ in eq. 16-14. This means, however, that the transformation that followed eq. 16-19 can be applied exactly to the expressions $c S Z/L$ and $c S W/L$, thus again leading to eq. 16-21.⁴ We repeat: In all these examples it is important that the skin effect should already be pronounced

⁴A. Sommerfeld [*Ann. Physik* (4) 24, 609 (1907)] has calculated the correction to eq. 16-13 needed for a normally conducting wire wound in the form of a coil. For pronounced skin effect, it consists of a real factor depending only on the spacing between successive windings of the coil and the radius of the wire. The same factor has to multiply $W = \text{Re}(Z)$, it can be taken over unchanged for the superconducting wire and so cancels in eq. 16-21 when forming the ratio W/W_s .

in the normal conductor. It is only if the smallest possible value of $|k|$, namely $|k_n|$, satisfies the condition $|k|R \gg 1$ that eq. 16-21 can be used for the cylinder.

(f) Let us reduce the temperature T starting from the transition temperature T_s . According to eq. 16-19 θ then decreases monotonically with λ , and the same is true of the function $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$ (Fig. 16-1). If finally the number $\omega \sigma \lambda$ becomes small compared with unity, owing to the decrease of λ , then also $\theta \ll 1$ and $\frac{1}{2} \sin \theta \sin \frac{1}{2} \theta$ has the value $(\omega \sigma \lambda)^{1/2}$. Therefore, according to eq. 16-21, we have

$$W = W_s \sqrt{\frac{\sigma_s}{2\omega} \omega^2 \sigma \lambda^{1/2}}$$

in agreement with eq. 16-17. W should decrease monotonically between this value and W_s provided the conductivity σ remains constant. However, the curves published by McLennan and co-workers [Chap. 1 (c)] for the resistance of tantalum as a function of temperature for frequency $\omega = 2\pi \cdot 1.4 \times 10^7$ per sec, i. e., the upper curve of Fig. 16-2 shows an initial maximum at which W is 4% higher than W_s and only after this does the expected decrease appear. If this maximum is real,⁵ it can only be interpreted as due to the conductivity σ starting to decrease at the transition temperature; according to eq. 16-21 the product $\sqrt{\sigma} W$ must decrease immediately below the transition temperature.

It is evidently impossible to determine both σ and λ as functions of T from a single empirical curve. But by using the empirical curve for W we can try to find a plausible form for σ as a function of T such that one derives a curve for λ that has a steep decline just below T_s , similar to that found in the experiments of Appleyard and Shoenberg with mercury [Chap. 1 (c)]. If W and σ are given for a certain T , then eq. 16-21 ascribes to this T a certain θ value, and eq. 16-19 a certain λ to this θ . We try the form

$$\frac{\sigma}{\sigma_s} = 0.6 + 0.4 \times e^{-5(T_s - T)} \quad (16-22)$$

⁵Recent work on resonant cavities instead of wires failed to show this maximum. J. C. Slater, E. Maxwell, P. Marcus, *Phys. Rev.* 76, 1332, (1949).

B. Pippard, *Proc. Roy. Soc. (London)*, 191, 370, 385, 399 (1947). 208, 195, 210, (1950).

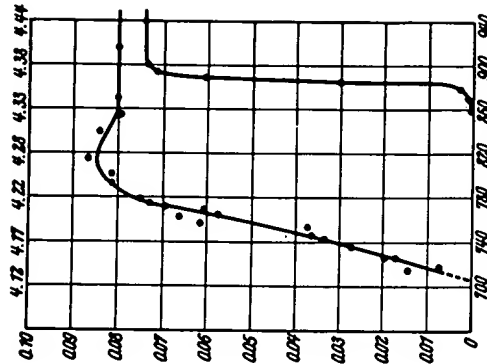


Fig. 16-2. Resistance of tantalum near the transition temperature.

according to which σ decreases to 0.6σ , within one degree and then remains constant. The empirical values of σ , differ. The finding of McLennan and his co-workers that the d-c resistance of tantalum at T_c is 0.07 of the resistance at 0°C leads to $\sigma_c = 1.30 \times 10^{10}$ per sec in Lorentz units, and we shall use this value. If it is wrong by a factor α , then all σ values have

to be multiplied by α and all λ values by $1/\alpha$, which does not change the form of the λ curve. The result of this calculation is shown in Fig. 16-3. The curve has indeed the expected form. Figure 11-3 gives the measurements of λ for mercury for comparison.

If this is considered a sufficient confirmation of the theory, we can proceed to ask how the W curve would be affected by going to higher frequencies. We see that the curve must be considerably raised by this at the lowest temperatures where W is still just noticeable, because of the factor ω^2 in eq. 16-18. It must also be raised at higher temperatures because according to eq. 16-19 θ increases with ω , and so therefore does the righthand side of eq. 16-21 at a given temperature (σ and λ fixed). However, this increase is less serious the greater $\omega\sigma\lambda$ already is, namely, the nearer T approaches T_c . As we already saw, θ has its greatest possible value $\pi/2$ for all frequencies at T_c itself, so that W remains equal to W_c there. The rise of the W curve up to W_c becomes less steep with higher frequencies, and the curve should rise appreciably above the zero level at lower temperatures as shown in Fig. 16-2.

(g) H. London measured the resistance of superconducting tin at frequencies of about 10^{10} cycles per second by producing eddy currents in an ellipsoidal specimen and calculating the heat produced by measuring the rate of evaporation of the helium bath. He also found that the high frequency resistance of the normal conductor passes continuously into that of the superconductor at the transition temperature, and that there is then a steep drop when we further decrease the temperature.

The considerations of this chapter become meaningless — as does the Maxwell theory itself — if the mean free path of the electrons becomes

comparable with or greater than the penetration depth. Deviations of this kind were first observed by Pippard⁶ and by Slater and co-workers.⁷ A theoretical treatment of this problem has been given by Reuter and Sondheimer⁸ and Slater *et al.*⁷

CHAPTER 17

Thermodynamics of the Transition between Normal and Superconducting Phases

(a) It was the Meissner effect that led to the idea that the superconducting and the normally conducting states are different phases of the same material in the sense that diamond and graphite are different phases of carbon. Earlier, when it was supposed that any arbitrary magnetic field could be "frozen in" within the interior of a superconductor (see Chap. 1) one had to presume an infinity of different superconducting states, and this excluded the phase idea. We know now, however, that the interior of a sufficiently thick superconductor in a stationary state is field free, protected by the thin surface layer, regardless of its history. Even if the metal is too thin to form this protective layer, the field in its interior is uniquely determined by the conditions imposed by the magnetic field in its neighborhood at the moment of interest, and independent of its previous history, always supposing this field to be stationary and changes of state as quasi-stationary just as we do in all thermodynamic arguments.

However, the superconducting and normally conducting phases are much more alike than are diamond and graphite. At all temperatures they have the same lattice structure, not only with regard to symmetry characteristics, but also the same lattice constants. Shape and volume are completely preserved during the transition. This point is essential to the following application of thermodynamics. It would not be if the transition between the two phases were effected by means of an intermediate vapor phase, a certain amount of one phase evaporating, the same amount condensing into the other solid phase. But in the present case one solid phase changes directly into the other, which is in contact with it; only the identity of the two lattices prevents the system from splitting into more or less minute fractions (being of the form single crystal \rightarrow polycrystal which would naturally exclude any reversibility).

⁶B. Pippard, *Proc. Roy. Soc. (London)*, 191, 370, 385, 399 (1947).

⁷J. C. Slater, E. Maxwell, P. Marcus, *Phys. Rev.* 76, 1332, (1949).

⁸G. E. H. Reuter and E. H. Sondheimer, *Proc. Roy. Soc. (London)*, 195 A, 336 (1948).

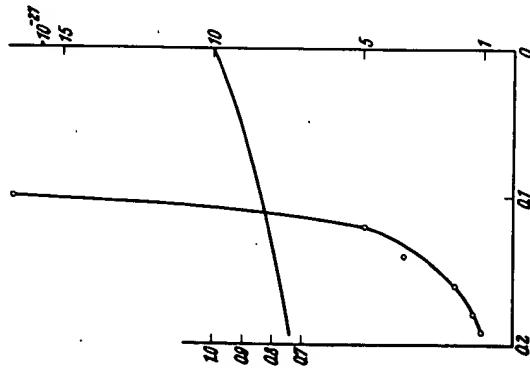


Fig. 16-3. Superconductivity constant and relative conductivity of tantalum as a function of temperature. Abscissa: temperature difference $T_c - T$, increasing toward the left. Ordinate: the steeper curve is the superconductivity constant in sec^{-1} given by the scale on the right-hand side; the flat curve is (σ/σ_c) given by the left-hand scale according to the assumption 16-22.

Incidentally Keesom and Kok¹ (for tellurium) and van Laer and Keesom² (for tin) have experimentally compared the heats of reaction during the transition both from the superconducting to the normal state and during the reverse transition and have found them equal, as required for reversibility.

A further assumption, supported indeed by the arguments of Chap. 5, is that the free energy of the magnetic field, including the superconduction energy is added to the free energy of the specimen, and so there is no free energy of interaction. This permits the following concept. The field is a "machine" exerting the forces on the surface of the superconductor that are given by the London stress system as discussed in Chap. 13. These forces perform work in so far as the surface is displaced, and this work serves to change the free energy of the material during isothermal displacements. The free energy of the field does not enter such a calculation, the internal changes of the "machine" being irrelevant for the energy balance in the specimen.

As shown in Chaps. 13 and 14 the force due to the field at a point where no current crosses the surface — the current lines being parallel to the surface — is a stress of amount $\frac{1}{2}(\mathbf{i} \cdot \mathbf{G})$ directed toward the interior of the superconductor. We shall calculate this example first.

(b) To do this we write f_s and f_N for the free energies ($f = e - Ts$) per mol of the superconductor and normal conductor respectively and V for the mol volume common to both phases, with $d\sigma$ a surface element of the superconductor and δn a virtual displacement of this element in the direction of its normal. δn is taken positive for displacements toward the interior of the superconductor as in Chap. 14 (f). It is necessarily positive wherever the superconductor borders upon empty space or a chemically different specimen, but δn can be negative if the superconductor joins on to a chemically identical normal conductor. For positive δn , $d\sigma \cdot \delta n/V$ mols of the superconductor change into normal conductor; the tension of the London stresses performs work $\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma$ (Chaps. 13 and 14) while the free energy of the material increases by $(f_N - f_s) d\sigma \cdot \delta n/V$. For negative δn the corresponding number of mols of normal conductor change into superconductor; the work done by the forces becomes negative. Naturally it is impossible for a single element alone to be displaced as the continuity of the boundary must be preserved, but an arbitrary infinitesimal displacement δn can be ascribed to any element $d\sigma$ of the surface. The total number of mols going over from one phase into the other is $\int \delta n \cdot d\sigma/V$ and the work done by the forces is

$$\delta A = \int \frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma \quad (17-1)$$

The corresponding change in free energy is

¹W. H. Keesom and J. A. Kok, *Physica*, 1, 503 (1934).

²P. H. van Laer and W. H. Keesom, *Physica*, 5, 993 (1938).

$$\delta F = \left[\frac{(f_N - f_s)}{V} \right] \int \delta n \cdot d\sigma \quad (17-2)$$

From the two principal laws of thermodynamics one concludes that for a spontaneous isothermal transition $\delta A > \delta F$. The necessary condition that a transition shall not occur is therefore

$$\delta A \leq \delta F$$

Applied to the displacement of the boundary this gives

$$\frac{1}{2} \int (\mathbf{i} \cdot \mathbf{G}) \delta n \cdot d\sigma \leq \left[\frac{(f_N - f_s)}{V} \right] \int \delta n \cdot d\sigma$$

Since δn can be either positive or negative, the inequality must reduce to equality: because if for some choice of δn the right-hand side were greater than the left side, it would be smaller for the opposite choice of δn . Furthermore, as δn is an arbitrary function of position on the surface, equilibrium must exist at every point:

$$\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) = \frac{(f_N - f_s)}{V} \quad (17-3)$$

This is the equilibrium condition for the boundary between super- and normal conductor. If δn is necessarily positive at the surface of a superconductor bordering empty space or a chemically different specimen the condition for conservation of superconductivity is

$$\frac{1}{2}(\mathbf{i} \cdot \mathbf{G}) \leq \frac{(f_N - f_s)}{V} \quad (17-4)$$

In this form both conditions are valid for "thick" superconductors with fully developed protective layers, as well as for the "thin" superconductors in which the magnetic field penetrates more or less completely. Since experiments almost always deal with "thick" superconductors these conditions are usually expressed instead in terms of the magnetic field at the surface, derived from the supercurrent there by the eq. 7-37 valid for "thick" superconductors. We define a field strength H_c by

$$\frac{1}{2} H_c^2 = \frac{(f_N - f_s)}{V} \quad (17-5)$$

The condition 17-3 for the boundary between super- and normal conductor reads

$$H = H_c \quad (17-6)$$

and the condition 17-4 for a boundary surface adjacent to empty space or a chemically different material:

$$H \leq H_c \quad (17-7)$$

This justifies our considering H_c defined by eq. 17-5 as a critical field. It is a necessary consequence of this theory that if H exceeds this value at any point of the free surface of a "thick" superconductor its superconductivity is destroyed.

If the magnetic field gives rise only to permanent magnetism and annular currents in superconductors, then according to Chap. 14 (e) the work δA performed by the field is equal to the decrease $(-\delta U)$ of the free energy of the field. Equation 17-3 states that in this case the sum of the free energy of the field and the specimen is conserved during the reversible phase transition. This statement however does not hold if ohmic currents are also produced, or if only ohmic currents are produced by the field. In this case the system (field plus specimen) is not a closed system. Additional electrostatic forces are required to fulfil the condition that the ohmic currents remain constant. If we wish to use the theorem of constant free energy we have to be quite clear about how the field is produced.

(c) These conclusions can also be derived for a "thick" superconductor from the volume forces exerted according to Chap. 13 by the Maxwell stresses, $[\mathbf{i} \times \mathbf{H}]/c$, on the supercurrent mechanism of the London theory. These forces are distributed over the thickness of the protecting layer. However, in the "thick" superconductor this protecting layer undergoes the virtual displacement δn as a whole without alteration of field or current distribution, so that we can calculate the work done by these forces per unit surface as the product of the resultant force per unit area times δn . As there is no field inside the layer, the resultant force is the pressure $\frac{1}{2} H^2$ of the lines of force on the outside, by Chap. 13. In this way we get the equilibrium condition

$$\delta A = \frac{1}{2} \int H^2 \delta n \cdot d\sigma \cong \left[\frac{(f_N - f_S)}{V} \right] \int \delta n \cdot d\sigma$$

and from this, the eqs. 17-6 and 17-7. This conclusion cannot be assumed so easily for thin superconductors where the field and current distribution change in a complicated fashion with a displacement δn of the surface.

This derivation has the advantage of being based more directly on the Meissner effect, i. e., the existence of the protective layer, than was the first derivation; but the latter is more general and can be used also for thin specimens.

(d) The free energies f_N and f_S are functions of the temperature T . We neglect their dependence on pressure or elastic stress because most experiments have been performed on strain-free specimens at one atmosphere which is effectively zero pressure. According to eq. 17-5 the critical value H_c is also a function of T . From thermodynamics we have³

$$s = - \frac{df}{dT} \quad (17-8)$$

for the entropy per mol, s , and we obtain eq. 17-5 by neglecting the extremely small changes in volume V at these temperatures in accordance with Nernst's theorem, thus:

$$s_N - s_S = - \frac{1}{2} V \frac{d(H_c^2)}{dT} = - V H_c \frac{dH_c}{dT} \quad (17-9)$$

³The specific heat does not depend on magnetic field (see discussion of Fig. 17-2) so we may write dH/dT instead of $(\partial H/\partial T)_H$.

This is the increase in entropy associated with the transfer of one mol from the superconducting to the normal state. Multiplying by T we get the amount of heat that has to be supplied with this transition:

$$Q = - \frac{1}{2} V T \frac{d(H_c^2)}{dT} = - V T H_c \frac{dH_c}{dT} \quad (17-10)$$

Further we have the following expression for the specific heat per mol at constant pressure:

$$c = T \frac{ds}{dT} = - T \frac{d^2 f}{dT^2} \quad (17-11)$$

So from eq. 17-9 we have

$$c_N - c_S = - \frac{1}{2} V T \frac{d^2(H_c^2)}{dT^2} = - V T \left[\left(\frac{dH_c}{dT} \right)^2 + H_c \frac{d^2 H_c}{dT^2} \right] \quad (17-12)$$

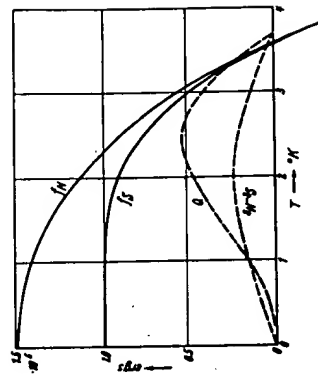


Fig. 17-1. Thermodynamic functions for tin below the transition temperature f_N and f_S are the free energies per mol in the normal and superconducting states. The curves split at the transition temperature 3.7°K . Only the difference $f_N - f_S$ has physical meaning. The upper dotted curve gives the heat Q in ergs per mol to be supplied during the transition of the superconductor into the normally conducting state. The lower dotted curve is the entropy difference $s_N - s_S$ in ergs per mol degree. The figures used come from eqs. 17-16 and 17-17:

$$f_N = -2.54 \times 10^3 T^4 - 8.40 \times 10^3 T^3 + 1.50 \times 10^5 \text{ erg/mol}$$

$$f_S = -5.92 \times 10^3 T^4 + 1.00 \times 10^5 \text{ erg/mol}$$

$$s_N - s_S = -1.35 \times 10^3 T^3 + 1.68 \times 10^4 T \text{ erg/mol deg}$$

$$Q = -1.35 \times 10^3 T^4 + 1.68 \times 10^4 T^2 \text{ erg/mol}$$

(e) These relations were first derived by Rutgers⁴ and by Casimir and Gorter.^{5,6} We shall discuss them now in the light of the free energy curves, f_N and f_S as functions of T , represented in Fig. 17-1. The slopes or tangents

⁴A. J. Rutgers, *Physica*, 1, 1055 (1934); 8, 999 (1936). See also P. Ehrenfest, *Proc. Roy. Acad. (Amsterdam)*, 86, 153 (1933).

⁵H. B. G. Casimir and C. J. Gorter, *Physica*, 1, 300 (1934).

⁶A formulation also valid for thin superconductors was given by Max von Laue, see Chap. 1, footnote 7, and Chap. 3, footnote 2 (f).

give the corresponding entropy, by eq. 17-8. H_c is zero at the transition temperature T_s , by definition, therefore $f_N = f_s$ there according to eq. 17-5, and the two curves coincide. Experiment shows that dH_c/dT is finite at T_s , so that by eq. 17-9 the two curves have a common tangent there. But by eq. 17-12 the curves differ in their second derivatives, i. e., curvature. For $T < T_s$ we always have $f_N > f_s$ according to eq. 17-5.

We cannot produce the curve of f_s above T_s because the superconductor does not exist there, not even as a phase that is unstable with respect to the normal conductor. We arrive at this conclusion first from the fact that the supercurrent constant becomes infinite at T_s , so that no value can be ascribed to λ above T_s . Secondly, from the fact that when $f_N - f_s$ is developed in a power series in $T - T_s$, it must start at the square term, so that the common point of the two curves would be a stationary point; f_N would then be greater than f_s above T_s , also, which is inconsistent with the whole concept of phase transitions. Approaching the transition from above, the free energy curve divides at T_s in such a way that the two branches originating at T_s have the same initial tangent.

Experience shows that H_c increases monotonically with decreasing temperature. According to eq. 17-5 the same must be true of $(f_N - f_s)$. At $T = 0$, $s_N - s_N$ must vanish by the Nernst theorem. Therefore by eq. 17-9 it follows that $(dH_c/dT)_{T=0} = 0$. The parabola drawn in Fig. 1-4 for H_c satisfies this condition and also the condition that dH_c/dT remains finite at T_s , without however being fixed by these conditions. On the other hand $dH_c/dT < 0$ and therefore by eq. 17-10 $Q > 0$: *The transition from the superconducting to the normally conducting state requires heat: the converse process liberates heat.* $Q = 0$ only at the absolute zero where also the factor dH_c/dT in eq. 17-10 vanishes as well as T , and at the transition temperature T_s where the factor H_c vanishes. Between these temperatures Q has at least one maximum. If the H_c -temperature curve is exactly parabolic as in Fig. 1-4 the only maximum is at $T = T_s/\sqrt{2} = 0.707 T_s$.

From the finite value of dH_c/dT at T_s we conclude by eq. 17-12 that $c_N < c_s$. However, in the neighborhood of the absolute zero where $dH_c/dT = 0$ and d^2H/dT^2 is still small, $c_N - c_s$ must be positive if d^2H_c/dT^2 is everywhere negative as in Fig. 1-4. In between there must be an intersection of the curves of c_N and c_s as functions of T . The entropy difference $s_N - s_s$ has a maximum at this point, by eq. 17-11. If the $H_c - T$ curve were exactly parabolic, this intersection would occur at $T = T_s/\sqrt{3} = 0.577 T_s$. At $T = 0$ both c_N and c_s are zero by the Nernst theorem.

In these calculations current density i and field strength H were expressed in Lorentz units. Transforming to electrostatic units H_c^2 has to be multiplied by the factor $1/4\pi$, according to eq. 3-10. Equations 17-5, 17-10, and 17-12 expressed in electrostatic units read:

$$\frac{V H_c^2}{8\pi} = f_N - f_s \quad (17-13)$$

$$Q = \left(\frac{V T}{8\pi} \right) \frac{dH_c^2}{dT} \quad (17-14)$$

$$c_N - c_s = - \frac{V T}{8\pi} \frac{d^2(H_c^2)}{dT^2} \quad (17-15)$$

According to eqs. 3-10 and 3-11 the general conditions 17-3 and 17-4 retain their form in the electrostatic system.

We are now in a position to derive from eq. 17-12 an equation that has often been used to check the theory against experimental evidence. By partial integration we have

$$- \int_{T_s}^{T_s} (c_N - c_s) dT = - \frac{1}{2} V \int_{T_s}^{T_s} T \frac{d^2(H_c^2)}{dT^2} dT = \frac{1}{2} V \left\{ T \frac{d(H_c^2)}{dT} \right\}_{T_s}^{T_s} - \int_{T_s}^{T_s} \frac{d(H_c^2)}{dT} dT \quad (17-16)$$

At T_s , $H_c = 0$ and $d(H_c^2)/dT = 0$. Using these expressions and eq. 17-10 to transform the right-hand side we obtain

$$-Q = \frac{1}{2} V H_c^2 + \int_{T_s}^{T_s} (c_N - c_s) dT \quad (17-16)$$

This equation expresses the energy principle for the following cycle: Consider one mol of substance:

1. Cool the superconducting phase from the transition temperature T_s to T . To effect this we have to supply the (negative) amount of heat

$$- \int_{T_s}^T c_s dT.$$

2. Transform the superconducting phase into the normally conducting phase isothermally by application of the magnetic field H_c ; this requires the supply of heat Q and the performance of work $\frac{1}{2} V H_c^2$ (see Chaps. 13 and 14).

3. Heat the normally conducting phase in the magnetic field H_c from T to T_s , for which we have to supply heat amounting to $\int_T^{T_s} c_N dT$.

4. Remove the magnetic field and transform the material at T_s into the superconducting state. This step requires no heat and no work. By equating the sum of all these amounts of heat and work to zero we obtain eq. 17-13.

If Fig. 1-4 is correct, H_c for lead increases to almost 1000 oersteds. V , the quotient of the mass of one mol, 207 g, and the density, 11.3 g/cm³, is about 18.5 cm³. Therefore $f_N - f_s = 7.5 \times 10^5$ erg = 1.8×10^{-2} cal.

For comparison we may mention that the difference of free energies of water and ice per mol is about 1.6×10^6 erg at 0° C and approximately

10^6 dynes/cm² pressure; and 4.6×10^8 erg at -20°C and about 1.9×10^9 dynes/cm².⁷

In the neighborhood of the transition temperature, where H_c is smaller by one or two powers of 10, $f_N - f_S$ is smaller by two to four powers of 10 and therefore quite small compared with the above values for water and ice.

Using the equation for the transition curve from which Fig. 1-4 was drawn,

$$H_c = a(T_s^2 - T^2), \quad a = 17.3 \text{ oersted/deg}^2, \quad T_s = 7.3^\circ$$

Calculating the maximum of the heat of transition at 5.2° and the difference between the specific heats at the transition temperature, we find:

$$Q_{\text{max}} = 6.2 \times 10^5 \text{ erg} = 1.5 \times 10^{-2} \text{ cal (lead)}$$

and

$$(c_N - c_S)T_s = 6.9 \times 10^5 \text{ erg/deg} = 1.6 \times 10^{-2} \text{ cal/deg (lead)}$$

These figures at least give some idea of the magnitude of the values under discussion.

(f) The Rutgers-Gorter-Casimir equations 17-5, 17-9, 17-10, and 17-12 have been confirmed for several metals. We may mention here the measurements on Zn by Keesom and van Laer.⁸ In Fig. 17-2 the points \circ show the experimental results for the molar heat found in the absence of a magnetic field. Starting above the transition temperature T_s , these points at first lie on the curve of c_N against T . At the transition temperature, 3.7°K , the points suddenly jump to higher values and trace the curve for c_S . The points \bullet were measured in the presence of a field of 299 oersteds, and the points Δ in a field of 139 oersteds. As these fields prevented the appearance of superconductivity, all these points lie on the curve for c_N which apparently does not depend on the field strength. This is an important confirmation of our assumption that the thermodynamic functions of the normal conductor are uninfluenced by a magnetic field. Although c_S lies much higher than c_N at the transition temperature, the two curves intersect each other at 1.9° as required in section (c).

The authors were able to represent the c_S curve by Debye's law for molar heat:

$$c_S = 464.5 \left(\frac{T}{\theta_S} \right)^3 \text{ cal deg}^{-1}, \quad \theta_S = 140^\circ \quad (17-17)$$

However, in order to obtain a good representation of c_N they had to add to the T^3 term a linear term in T :

$$c_N = 464.5 \left(\frac{T}{\theta_N} \right)^3 + 4 \times 10^{-4} T \text{ cal deg}^{-1}, \quad \theta_N = 185^\circ \quad (17-18)$$

In fact, even with this additional term there are still discrepancies above 3.5°K . The second term may be interpreted as the specific heat of the conduction electrons on the Sommerfeld theory of metallic conductivity.

⁷ Calculated as the product of pressure and change of volume.

⁸ W. H. Keesom and P. H. van Laer, *Physica*, 5, 193 (1938). The value $\theta_S = 140^\circ$ was taken from their Fig. 2.

The difference $c_N - c_S$ is thus of the form $\alpha T^3 + \beta T$. This leads to the parabola for H_c as a function of T , by eq. 17-12 and the conditions $dH_c/dT = 0$ at $T = 0$ and $H_c = 0$ at $T = T_s$. The authors also emphasize that eq. 17-12 is well satisfied if their measurements are combined with those of de Haas and Engelke⁹ on H_c .

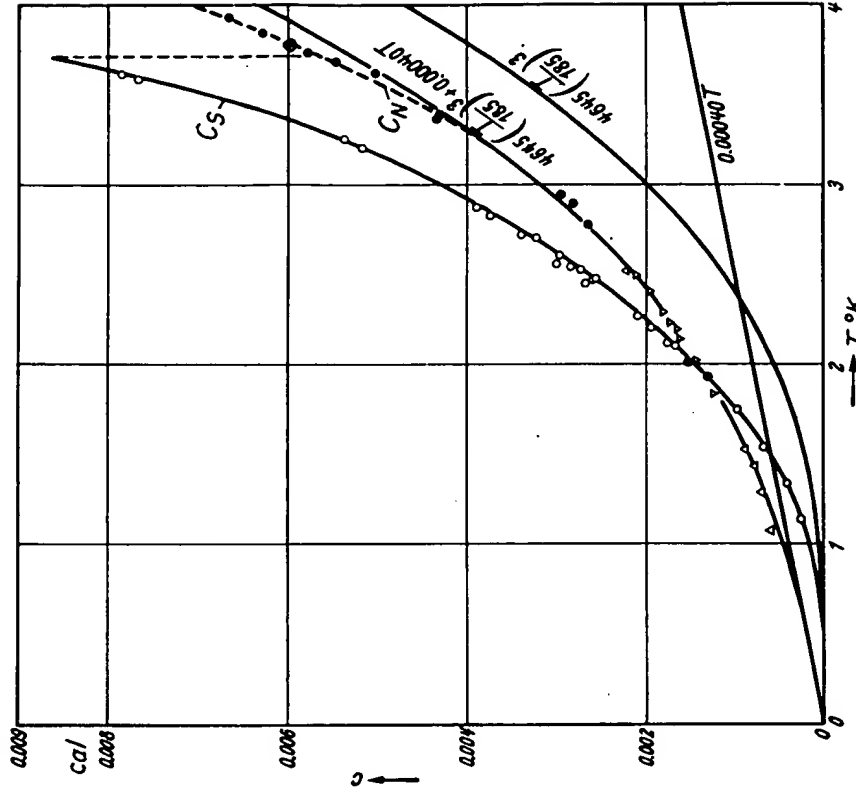


Fig. 17-2. Atomic heat of normal and superconducting tin as a function of temperature.

The jump in the atomic heat of tin at T_s is 1.26×10^5 erg/deg $= 3.0 \times 10^{-3}$ cal/deg, according to Fig. 17-2, and so considerably smaller than that found in lead [section (e)]. In addition to the f_N and f_S curves in Fig. 17-1 we have also plotted the entropy difference, using the values from eqs. 17-17 and 17-18:

⁹ W. J. de Haas and Miss A. D. Engelke, *Physica*, 4, 325 (1937).

$$-(s_N - s_S) = \int_T^{T_c} \frac{1}{T} (c_N - c_S) dT. \quad (17-19)$$

and also the heat of the transformation $Q = T(s_N - s_S)$.

Keesom and van Laer¹⁰ examined the validity of eq. 17-3 by measuring the heat of transformation Q and the specific heats of tin. They find agreement between calculated and measured values of Q to within 5% in the least favorable case. The confirmation of eq. 17-19 in the same paper shows that the assumption of a reversible phase transition is justified.

(g) A homogeneous magnetic field does not generally need to have the full strength H_c in order to quench the superconductivity of any body placed in it. As shown in Chaps. 9 to 11 for many examples, and depicted in Fig. 1-5, the distortion of the field by the superconductor produces an intensification of the field at the surface of that body. This suffices for the quenching of the superconductivity if the intensification raises the field at some point to beyond H_c . If we write a for the ratio of the maximum field strength at the surface to the field strength at a great distance from the specimen, the critical value of this latter field is H_c/a . In the sequel we must distinguish carefully between this value, depending on the form of the specimen, and the critical H_c that depends only on the material of the specimen and the temperature.

For a "thick" elliptical cylinder with axes a and b , the a axis forming the angle θ with the direction of the field we have, by eq. 10-24:

$$a = \left(\frac{1}{a} + \frac{1}{b} \right) \frac{1}{\sqrt{a^2 \sin^2 \theta + b^2 \cos^2 \theta}} \quad (17-20)$$

The intensification factor a therefore varies with θ between $1 + b/a$ and $1 + a/b$. This has been confirmed at least qualitatively by de Haas and Casimir-Jonker [Chap. 1 (f)]. For the thick circular cylinder $a = 2$, for the "thick" sphere $a = 3/2$, see Chap. 11.

CHAPTER 18

The Critical Magnetic Field for Thin Superconductors

(a) It is only for "thick" superconductors that the field strength H_c defined in eq. 17-5 is a critical value exceeding which at any point of the free surface would destroy the superconductivity. Equation 7-37 between current density and magnetic field strength at the surface holds only for a fully developed protective layer. For "thin" superconductors in which the protective layer is not fully developed, we have to go back to the more

¹⁰ W. H. Keesom and P. H. van Laer, *Physica*, 3, 371 (1936).

general equations 17-3 and 17-4. These equations, remembering eq. 17-5, can be written:

$$\begin{aligned} (i_s \cdot G) &= H_c^2, & \text{equilibrium condition for the boundary between} \\ & & \text{superconductor and normal conductor} \\ (i_s \cdot G) &\leq H_c^2, & \text{condition for preserving superconductivity} \\ & & \text{at a free surface} \end{aligned} \quad (18-1)$$

In what follows we discuss cubic crystal superconductors with $(i_s \cdot G) = \lambda i_s^2$. However, the results are qualitatively valid for other forms.

Consider two geometrically similar thin superconductors of the same material and at the same temperature such that the linear dimensions of the smaller specimen can be obtained from those of the larger one by multiplication by the factor $\alpha < 1$. Let the two specimens be placed in the same homogeneous magnetic field H^0 ; then the ratio of the current density i_s in the smaller specimen to that at the corresponding point in the larger specimen is, according to Chap. 7 (f) equal to α .

Since i_s is proportional to H^0 we have to increase H^0 by the factor α^{-1} to get the same stress $\frac{1}{2} \lambda i_s^2 = \frac{1}{2} H_c^2$ at corresponding points on the surface of the smaller specimen. The critical value of H^0 needed to quench superconductivity increases by the factor α^{-1} when the dimensions of the specimen are decreased by the factor α . The smaller the disturbance of the field caused by a small superconductor, the less it is influenced by the field.

(b) We shall prove this for a few examples. For a plane parallel plate of thickness $2d$ with field strength H^0 at both sides we have by eq. 7-18

$$\lambda i_s^2 = (H^0)^2 \tanh^2 \beta d$$

According to eq. 18-1 the superconductivity is quenched at the critical value

$$H^0 = H_c \coth \beta d > H_c \quad (18-2)$$

For a "thick" plate this is approximately

$$H^0 = H_c (1 + 2e^{-2\beta d}) \quad (18-3)$$

and for a "thin" one

$$H^0 = H_c \frac{[1 + (\beta d)^2/3]}{\beta d} \quad (18-4)$$

The denominator βd corresponds to the factor α in the theorem of (a).

The current density at the surface of a cylinder of radius R in a longitudinal field H^0 is, according to eq. 10-2, given by:

$$\lambda (i_s)^2 = (H^0)^2 \left[-\frac{i I_1(i\beta R)}{I_0(i\beta R)} \right]^2$$

The critical value is therefore

$$H^0 = H_c \left[\frac{I_0(i\beta R)}{I_1(i\beta R)} \right] > H_c \quad (18-5)$$

By using eq. 16-15 for the ratio of the Bessel functions for large values of βR we find

$$H^0 = H_c \left(1 + \frac{1}{2\beta R} \right) \quad (18-6)$$

For small values of βR , however, the series 8-6 gives

$$H^0 = 2H_c \frac{1 + \frac{1}{8}(\beta R)^2}{\beta R} \quad (18-7)$$

For a cylinder in a transverse field the current density at the surface is, by eq. 10-16, a maximum at $\theta = \frac{1}{2}\pi$. At this angle

$$(\mathbf{i}_s)^2_{R, \frac{1}{2}\pi} = 4(H^0)^2 \left[-\frac{\epsilon I_1(\epsilon\beta R)}{I_0(\epsilon\beta R)} \right]^2$$

This value is four times the value for longitudinal fields. Therefore we have simply to divide the right-hand sides of eqs. 18-5, 18-6, and 18-7 by 2 to get the corresponding results for the transverse field.

The current density at the surface of a sphere of radius R has a maximum on the equatorial plane $\theta = \frac{1}{2}\pi$. According to eqs. 11-1, 11-9, and 11-5 we have

$$\lambda (\mathbf{i}_s)^2_{R, \frac{1}{2}\pi} = (H^0)^2 \left\{ \frac{3}{2} [\coth \beta R - (\beta R)^{-1}]^2 \right\}$$

A homogeneous field can therefore be increased without destroying the superconductivity only as far as the critical value:

$$H^0 = \frac{3}{2} H_c [\coth \beta R - (\beta R)^{-1}]^{-1} > \frac{2H_c}{3} \quad (18-8)$$

This means for $\beta R \gg 1$, up to

$$H^0 = \frac{2}{3} H_c \left(1 + \frac{1}{\beta R} \right) \quad (18-9)$$

while with $\beta R \ll 1$, up to

$$H^0 = 2H_c \frac{1 + \frac{1}{15}(\beta R)^2}{\beta R} \quad (18-10)$$

The denominator βR in eqs. 18-7 and 18-10 again corresponds to the a factor in the theorem of section (a).

(c) We follow these examples by three paradoxes. At the two boundaries $z = \pm d$ of a plane parallel plate of thickness $2d$ carrying current i per centimeter, the current density and magnetic field are given by eq. 7-21:

$$|\mathbf{i}_s| = \frac{1}{2} \beta I \coth \beta d, \quad |\mathbf{H}_y| = \frac{I}{2c}$$

The critical value of i that quenches superconductivity is such that $\lambda \mathbf{i}_s^2 = H_c^2$. Therefore the critical current and the corresponding field intensity are respectively

$$i = 2c H_c \tanh \beta d, \quad |\mathbf{H}_y| = H_c \tanh \beta d \quad (18-11)$$

The critical current therefore decreases with decreasing βd finally going to zero; the same is true of the corresponding magnetic field. The mean critical current density, however, namely,

$$\frac{i_s}{2d} = \frac{H_c}{\sqrt{\lambda}} \frac{\tanh \beta d}{\beta d} \quad (18-12)$$

increases to a maximum value $H_c/\sqrt{\lambda}$.

The current density at the surface of a wire of radius R carrying current i is, by eq. 8-9

$$(\mathbf{i}_s)_R = \frac{\beta I}{2\pi R} \frac{\epsilon I_0(\epsilon\beta R)}{I_1(\epsilon\beta R)}$$

To find the maximum possible supercurrent we must put $\lambda \mathbf{i}_s^2 = H_c^2$. This gives the maximum possible mean current density

$$\frac{i_s}{\pi R^2} = \epsilon \frac{H_c}{\beta \sqrt{\lambda} R} \frac{I_1(\epsilon\beta R)}{I_0(\epsilon\beta R)} \quad (18-13)$$

The ratio of the Bessel functions decreases more slowly than βR , the mean current density therefore increases, but more slowly than $(\beta R)^{-1}$. In particular for large βR we have

$$\frac{i_s}{\pi R^2} = \frac{2H_c}{\beta \sqrt{\lambda} R} \left(1 - \frac{1}{2} \beta R \right) \quad (18-14)$$

and for small βR

$$\frac{i_s}{\pi R^2} = \frac{H_c}{\sqrt{\lambda}} \left[1 - \frac{1}{8} (\beta R)^2 \right] \quad (18-15)$$

$H_c/\sqrt{\lambda}$ is again the maximum possible current density. The magnetic field produced by this maximum current at the surface of the wire is

$$\frac{i_s}{2\pi c R} = -\frac{H_c \epsilon I_1(\epsilon\beta R)}{I_0(\epsilon\beta R)} \quad (18-16)$$

and is thus smaller than H_c , and the more so the smaller βR , vanishing with βR . These examples do not actually contradict the theorem of section (a), because in both these cases the superconductor was not put into an already existing field. The field outside would not exist without the current i .

The above results can easily be demonstrated and generalized. The maximum possible current load is characterized by the fact that the current density attains the value $H_c/\sqrt{\lambda}$ for which the stress is $\frac{1}{2} \lambda \mathbf{i}_s^2 = \frac{1}{2} H_c^2$ at one or more points on the surface (in both the above examples actually over the whole surface). The mean current density required for this in a "thick" superconductor is actually very small compared with $H_c/\sqrt{\lambda}$ because of the extended protected region beneath the protecting layer. However, the mean density for a very "thin" superconductor is equal to $H_c/\sqrt{\lambda}$ because the current is uniformly distributed over the whole cross section. It can never increase beyond this value under any circumstances,

because according to Chap. 7 the maximum current density is always at the surface. As the cross section decreases toward zero, the maximum possible current and the magnetic field at the surface produced by this current also decrease toward zero. This is shown by eqs. 18-11 and 18-12 for a wire and eqs. 18-14, and 18-16 for a plate.

(d) The third of the mentioned paradoxes is of a different kind. If the bore of a hollow thick cylindrical superconductor contains a magnetic field H^0 , then according to eqs. 10-7 and 10-6 the current on the walls is given by

$$\lambda i_0 r^2 = (H^0)^2 \left[\frac{H_1(\epsilon \beta R)}{H_0(\epsilon \beta R)} \right]^2$$

To make this equal to H_c^2 we must have¹

$$H^0 = -H_c \frac{H_0(\epsilon \beta R)}{H_1(\epsilon \beta R)} \quad (18-17)$$

The factor multiplying H_c is less than unity and is smaller the smaller βR . Whereas for large βR we have

$$H^0 = H_c \left(1 - \frac{1}{2\beta R} \right) \quad (18-18)$$

for indefinitely decreasing values of βR the maximum possible value of H^0 goes to zero according to the equation

$$H^0 = -H_c \beta R \log \beta R$$

This decrease with decreasing βR is again no contradiction to section (a), as we are not considering a "thin" superconductor.²

As already mentioned in Chap. 12 (g), it can happen that, upon cooling down a normally conducting metal in a magnetic field, at first only an annular part of the specimen becomes superconducting. Normal conductivity remains within the bore of this ring, and a number of lines of force, or rather a certain flux of induction $\int \mathbf{B}_n \cdot d\sigma$ is present there. This flux must remain constant (Chap. 12) with further progress of the cooling. If the bore becomes smaller, the field intensity must increase. We see therefore that the bore cannot become arbitrarily small. The critical value of the field strength decreases with the decreasing dimensions of the bore, so that in any case a state will be reached where any further shrinking of the bore will cause the magnetic field to exceed this critical value.

(e) We now come to the measurements of the critical value for "thin" superconductors. Pontius [Chap. 1 (c)] measured the critical values of a longitudinal field for lead wires at 4.2°, i. e., 3.1° below the transition temperature. The radii of the wires were of the order of magnitude 10⁻⁴ cm

¹ $H_0(\epsilon \beta R)$ and $-H_1(\epsilon \beta R)$ are positive as mentioned in Chap. 10.

² The equations of section (b), (c), and (d) were first given by M. v. Laue in the paper already quoted: *Ann. Physik*, 82, 71, 253 (1938). An error in sign in that paper led to a wrong result for the cylinder in a transverse field. The numerical values used in section (e) are also taken from that paper.

to 10⁻³ cm. Figure 18-1 shows his observations compared with a theoretical curve calculated, not from eq. 18-6, but by the somewhat more exact equation³

$$\left(\frac{H_c}{H^0} \right)^2 = 1 - \frac{1}{\beta R} + \text{terms in } \frac{1}{(\beta R)^3} \quad (18-19)$$

It has been assumed that $H_c = 537$ oersteds, and then that $\beta = 4.78 \times 10^4 \text{ cm}^{-1}$ to yield by eq. 6-7 the value for λ :

$$\lambda = 4.8 \times 10^{-31} \text{ sec}^2 \text{ in Lorentz units}$$

or by eq. 6-8 the 4π times greater value

$$\lambda = 6.0 \times 10^{-30} \text{ sec}^2 \text{ in esu.}$$

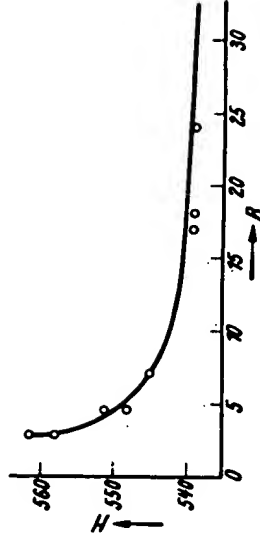


Fig. 18-1. The limiting field strength H^0 in Oersts as function of the radius R of the wire (in 10⁻⁴ cm units) for lead at 4.2° K. The theoretical curve according to eq. 18-19 and the points observed by Pontius.

This good agreement between the calculated and observed values not only supports the theory in general, but also supports the orders of magnitude for β and λ proposed by F. London from quantum mechanical considerations. This calculation was made in 1938 and was the first one to be based on observational data.

There are also data for thin films. Shalnikov [Chap. 1 (c)] used a lead film 1.4 × 10⁻⁸ cm thick and a tin film 1.1 × 10⁻⁵ cm thick and found

³ From eq. 8-7

$$-\frac{\epsilon I_1(\epsilon X)}{I_0(\epsilon X)} = \frac{d [\log I_0(\epsilon X)]}{d X}$$

and by eq. 16-10

$$I_0(\epsilon X) = \frac{e^X (1 + 1/8 X)}{\sqrt{2\pi X}}$$

therefore

$$-\frac{\epsilon I_1(\epsilon X)}{I_0(\epsilon X)} = 1 - \frac{1}{X} + \text{terms in } \frac{1}{X^3}$$

Equation 18-6 should be more exactly

$$H^0 = H_c \left[1 + \frac{1}{2\beta R} + \frac{3}{8(\beta R)^3} \right]$$

that the critical magnetic field strength required to quench superconductivity was far higher than the critical value H_c found for "thick" films. However, the critical current load was much smaller than that calculated from H_c on the Silsbee hypothesis. He found these results for temperatures ranging over several degrees. They correspond qualitatively with the results of sections (b) and (c). They agree also qualitatively with those of Appleyard and Misener [Chap. 1 (c)] on the critical magnetic field values in mercury films from 4×10^{-6} to 1×10^{-4} cm thick. Shalnikov's results do not seem suitable for a quantitative check of eq. 18-2 or the determination of β because they do not agree quantitatively with the measurements of Appleyard, Bristow, and H. London [Chap. 1 (c)] for mercury films of a similar thickness. The last mentioned authors, however, arrived at an estimate of the relative value of β at any T to its value at 2.5° K in the following manner. As the critical value depends only on the product βd , they selected from among their data at different temperatures and thicknesses those which yielded the same critical value. Then βd must have the same value for all these cases; thus

$$\frac{\beta_T}{\beta_{2.5}} = \frac{d_{2.5}}{d_T}$$

But by eq. 6-7 β is inversely proportional to the square root of λ . In this way the authors found the relation between $\sqrt{\lambda}$ and T shown in Fig. 11-3, which also shows in a striking manner the results of a completely different determination made by Shoenberg [Chap. 11 (d)].

Incidentally all these measurements of the critical magnetic field when used in eq. 18-2 to calculate β lead to the expected result that, sufficiently far below the transition temperature, β has the order of magnitude of 10^5 cm^{-1} .

(f) The whole argument of Chaps. 17 and 18 depends on the condition emphasized in Chap. 17 (a) that no current shall be entering or leaving the superconductor at the points of interest on its surface. It is only under this condition that the London stresses give rise to the tensile stress $\frac{1}{2} \lambda i^2$ toward the interior of the superconductor. Where there is a current being supplied from outside and where i has no tangential component, the tension is replaced by a pressure of the same amount directed outwards. In general if both normal and tangential components of i exist, the force is inclined to the surface. The tangential component is exactly zero only at a few points on the surface of a "thick" superconductor. For example we saw in Chap. 8 (c) that in a superconducting cylinder of radius R to which a current is supplied through a normally conducting cylinder of the same thickness, the tangential component i_t almost everywhere over the interface greatly exceeds the normal component i_n as long as $\beta R \gg 1$. Only on the axis $r = 0$ and at the circumference $r = R$ is $i_t = 0$. Only in areas around these radii of extension β^{-1} is $i_t \gg i_n$.

For a "thin" cylinder or more generally a "thin" superconductor of arbitrary cross section in which the supercurrent, like the ohmic current

in the normal conductor, spreads uniformly over the cross section [Chap. 7 (a)], the tangential component at the interface vanishes. At such points, provided the normally conducting leads consist of the same material as the superconductor, thermodynamic equilibrium between the two phases would depend on the condition (compare eq. 17-3)

$$-\frac{1}{2} (i \cdot G) = \frac{(f_N - f_S)}{V}$$

This condition cannot be satisfied, because at any temperature at which the superconductor can exist at all, i.e., any temperature below T_c , $f_N - f_S > 0$ according to Chap. 17 (e) and Fig. 17-1 whereas $(i \cdot G)$ is positive according to Chap. 3. The current at the interface can therefore only strengthen the tendency of the superconductor to grow at the expense of the normal conductor. Certain as yet unexplained relaxation phenomena which often blur the sharpness of the phase transition may be related to this point.

CHAPTER 19

The Intermediate State

(a) If the superconductivity of a specimen is quenched isothermally by an increasing external magnetic field, it does not transform immediately and completely into the normally conducting state. The nearest approach to a sudden complete transition is found with straight wires in longitudinal fields. However, even in this case the resistance does not change from zero to its final value in one single jump. The transition is by no means continuous, but takes place in several separate jumps. Thus if, following Justi¹ one wraps around the specimen an induction coil connected with an oscillograph or a telephone, and subjects the specimen to a continuously increasing magnetic field, one observes current impulses caused by sudden large changes in the flux of induction.

In other cases where the transition is much slower it can be followed through all its intermediate stages by placing minute bismuth wires inside cavities in the specimen and measuring their resistance as a function of the external field, as was done by de Haas and his collaborators. The resistance of bismuth changes in a known manner with the local magnetic field strength. This arrangement, which naturally is limited to thick superconductors, demonstrates the gradual penetration of the external field. It is impossible for a normally conducting shell to form either completely or partly round a superconducting core. The thermodynamics of Chap. 17 requires the existence of the critical magnetic field H_c corresponding to the prevailing

¹E. Justi, *Physik Z.*, 48, 130 (1942); *Ann. Physik*, 48, 84 (1942).

temperature at every point on the boundary between any such normal envelope and the core. On the other hand, the lines of force, according to electrodynamics, must be parallel to the boundary surface. These two requirements are mathematically inconsistent.

(b) In the first place it is out of the question for the normally conducting shell to enclose the superconducting core completely. There must exist places (either curves or at least points) on the boundary surface where the incident lines of force divide sharply into two lines parallel to the surface. (For a spherical core this would occur at the poles, see Fig. 1-5.) The field strength at these points is zero according to potential theory because the field direction is indefinite, and so cannot equal H_c .

Let us confine ourselves for the moment to two-dimensional problems. Let the boundary of the core S consist of two parts S_1 and S_2 ; at S_1 the core borders either on empty space or on a normal conductor of chemically different material, and at S_2 on the normally conducting shell. Both S_1 and S_2 may consist of several separate sections. We assume each section to be an analytic curve i. e., they can be represented by equations of the form $x = f(s)$, $y = g(s)$ where f and g are analytic functions.

At each point where a section of S_1 meets the adjacent section of S_2 it is not permissible for them to form an angle with each other. Such an angle would make a kink in S ; if the kink were re-entrant the field strength, according to potential theory, would be zero; if the kink were raised (convex), the field would be extremely large (mathematically infinite); in any case it could not be equal to H_c at such kinks. The above parametric representation therefore holds uniformly over the whole boundary curve S , and therefore H on the boundary must also be an analytic function of the parameter s . As it is constant and equal to H_c over all parts of S_2 , it must also be equal to H_c over S_1 in spite of the fact that it must also be zero at some points.

The same inconsistency is found in the three-dimensional case. We can ascribe to any part of the boundary, whether it belongs to S_1 or to S_2 , an analytical representation in terms of two parameters: $x = f(s, t)$, $y = g(s, t)$, $z = h(s, t)$. No singularities are permitted at any point where sections of S_1 and S_2 touch, because they would cause zeros or infinities in H . Therefore the analytical representation holds uniformly over the whole boundary S . Then H is also an analytical function of s and t . Because it is constant and equal to H_c over S_2 , it must also be constant over S_1 in spite of the fact that places must exist where $H = 0$.² So if a piece of material cannot be either normally conducting as a whole nor superconducting, it must be in an "intermediate state" representing a mixture of alternating superconducting and normally conducting regions.

The difficulty discussed above for thick superconductors does not exist for small superconducting regions dispersed through a normal conductor, because such small regions do not disturb the magnetic field, according to

Chap. 7, and are themselves barely affected by the field, according to Chap. 18.

These conclusions are confirmed by an experiment by Shubnikov and Nachutin.³ They quenched the superconductivity of a sphere in a magnetic field and measured the electric resistance parallel and perpendicular to the external field before the sphere had become completely normally conducting. Long after resistance had appeared in the direction perpendicular to the field, they could find no resistance in the direction parallel to the field. This is difficult to explain except in terms of coexisting normal and superconducting regions. It suggests, moreover, that the superconducting regions are much more extended in the direction of the field than in the transverse direction. This fits in with the argument of Chap. 18 (b) according to which a cylinder or any other elongated specimen loses its superconductivity much more easily in a transverse field than in a longitudinal one.

(c) The earliest method of recognizing superconductivity was to observe the disappearance of the d-c resistance. However this method is hardly suitable for distinguishing between the superconducting and the intermediate states because the normally conducting regions will not participate in carrying the current so long as the current can find a closed path through the superconducting regions. A far better criterion for the break down of the superconducting state is the disappearance of the Meissner effect, i. e., the appearance of a magnetic field within the interior of the specimen. In this way it is possible to understand why the first measurable resistance of a wire in a transverse field has been observed at $H^0 = 0.58 H_c$,⁴ whereas according to theory [Chap. 18 (b)] and the experiments to be mentioned immediately, superconductivity is already destroyed when $H^0 = 0.50 H_c$.

In order to observe the field penetration, de Haas and Casimir-Jonker⁵ inserted minute bismuth wires, as described above, in holes in a tin wire 0.7 cm in diameter, see Fig. 19-1. They measured the increase of resistance of the bismuth wires while gradually increasing the external magnetic field H^0 . Figure 19-2 shows the results when the plane of the wires is perpendicular to the field H^0 ; Fig. 19-3 when it is parallel. The critical value H_c can be recognized in both diagrams at the point where the resistance curves meet the resistance curve of a bismuth wire exposed to the external field H^0 , and indicated in Fig. 19-2 by the dotted line. This point is where the specimen allows the external field to penetrate it completely. In Fig. 19-2

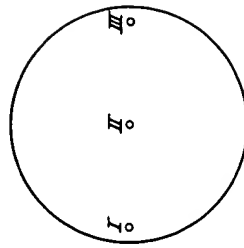


Fig. 19-1. Cross section through tin cylinder with bismuth probe wires inserted at I, II, and III. (After W. J. de Haas and J. M. Casimir-Jonker.)

³L. Shubnikov and J. Nachutin, *J. Exp. Theoret. Phys. (U.S.S.R.)*, **7**, 566 (1937).

⁴W. J. de Haas, J. Voogd, and J. M. Casimir-Jonker, *Physica*, **1**, 281 (1934).

⁵W. J. de Haas, and J. M. Casimir-Jonker, *Physica*, **1**, 291 (1934).

²M. v. Laue, *Physik. Z.*, **48**, 274 (1942).

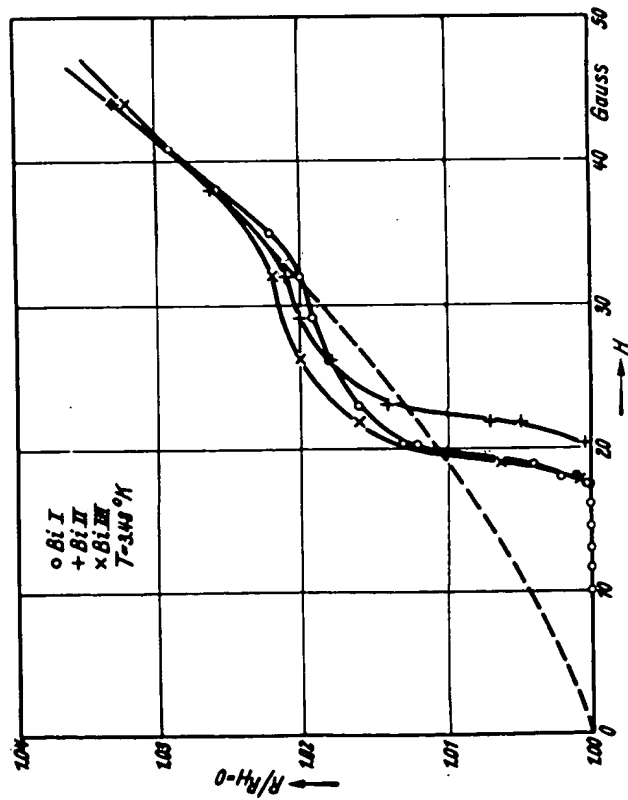


Fig. 19-2. Increase of resistance in the bismuth probe wires due to penetration of a magnetic field normal to the plane of the wires.

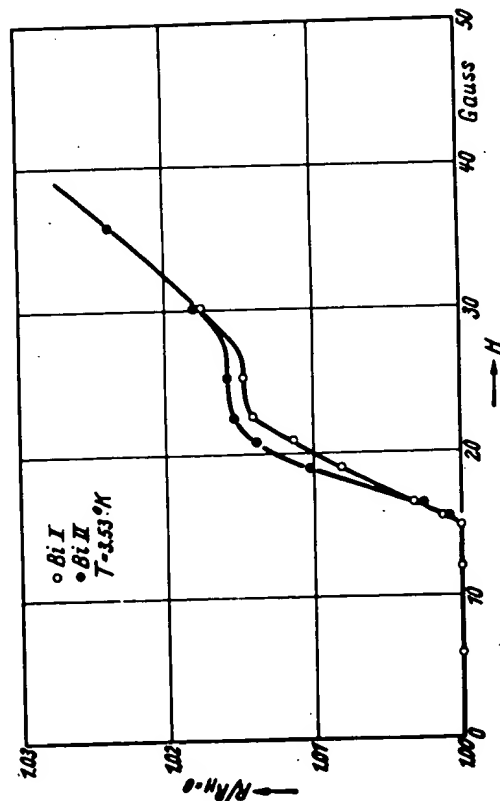


Fig. 19-3. Increase of resistance in the bismuth probes due to penetration of a magnetic field parallel to the plane of the wires.

H_c falls at about 36 oersteds; in Fig. 19-3 at about 30 oersteds because of the slightly higher temperature. One sees that the first sign of the field penetration occurs in both diagrams at the field $H^0 = \frac{1}{2} H_c$, i. e., at 18 and 15 oersteds respectively, as required by theory. The wire II was placed in the axis of the wire, so the fact that its curve reacted only at 20 oersteds does not alter the fact that both the wires I and III, placed nearer the outside of the wire, show the breakdown of superconductivity already at 18 oersteds.

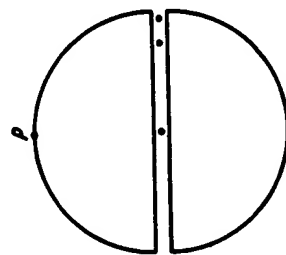


Fig. 19-4. Cross section of a tin sphere cut across an equatorial plane with bismuth wires inserted at the points shown. (After W. J. de Haas and O. A. Guineau.)

Fig. 19-5. Magnetically induced isothermal transition from super- to normal conduction in a single crystal tin sphere. Points marked A, B, C represent magnetic field strengths shown by the bismuth probes of Fig. 19-4, D the field strength at the pole P of the sphere.

The theory has been confirmed more exactly for the case of a sphere where, according to Chap. 18 (b) the critical value should be $H^0 = 2 H_c/3$. de Haas and Guineau⁶ cut a tin sphere (1.65 cm in diameter) into two hemispheres and placed them 0.03 mm apart (Fig. 19-4). In the space between the two halves they placed three bismuth wires, one in the center, the second 0.55 cm and the third 0.75 cm from the center. The field strengths calculated from the resistance decrease in the bismuth wires are shown in Fig. 19-5 as a function of H^0 which in this experiment was perpendicular to the plane of the cut. The magnetic field strength at the pole P of the sphere is also plotted. All four curves coincide exactly. They start at 24 oersteds, and at 36 oersteds they join the straight line $H = H^0$, indicating that the protective influence of the tin sphere has completely disappeared. Thus the critical value H_c is 36 oersteds, and the limiting value H^0 for superconductivity is $2/3 H_c$.

⁶W. J. de Haas and O. A. Guineau, *Physica*, 8, 182 (1936).

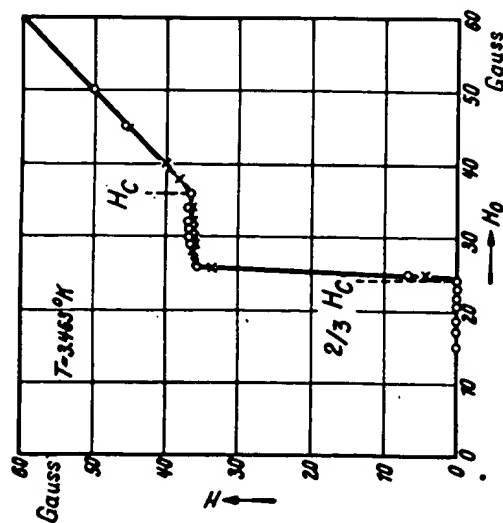


Fig. 19-6. Magnetically induced isothermal transition from super- to normal conduction of a single crystal tin sphere. The field strengths are measured in a hole bored through the center of the sphere parallel to the field.

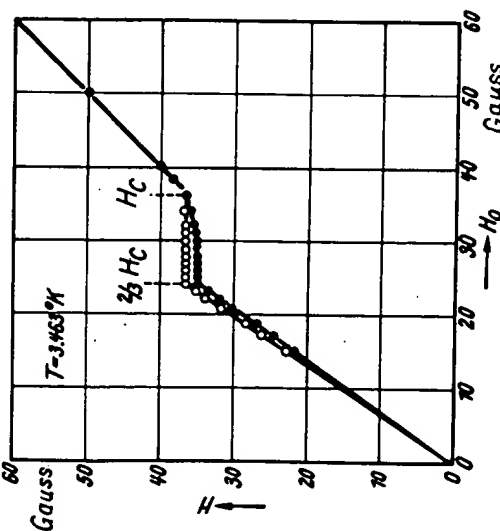


Fig. 19-7. Magnetically induced isothermal transition from super- to normal conduction in a single crystal tin sphere. \circ -field strength exactly on the equator of the sphere; \bullet -field strength at a point on the plane of the equator slightly outside the sphere.

This is further confirmed by experiments re-presented in Fig. 19-6, in which the bismuth wires were placed inside a channel parallel to the field through the center of the sphere to measure the field penetration. The field jumps almost discontinuously to the value 36 oersteds when the external field reaches the value 24 oersteds, and remains practically constant until H^0 also reaches the value 36 oersteds. From then on the sphere no longer disturbs the field, and it follows the line $H = H^0$.

Figure 19-7 explains why the field jumps immediately to 36 oersteds in spite of the fact that H^0 is still smaller than this value. In this experiment two bismuth wires were placed in the equatorial plane, one exactly on the equator of the sphere (which was not cut like the one in Fig. 19-6), the other a little above the surface of the sphere. In this case the measured field H follows a straight line $H = 3H^0/2$ and shows the intensification of the field at the equator of a superconducting sphere [Chap. 11 (b)]. At $H^0 = 24$, and $H = 36$ oersteds, however, the superconductivity breaks down, and H at first remains constant at this value as shown in Fig.

19-6. As soon as H^0 also reaches 36 oersteds the undisturbed field H^0 exists throughout the sphere, as shown again in this diagram.

The experiments represented in Figs. 19-4 and 19-5 have been repeated by Meshkovski and Shalnikov⁷ with a considerably narrower slit. Also instead of three fixed bismuth wires they used a movable bismuth probe which they displaced continuously along the diameter, registering field strengths at each position. For wider slits and relatively thick bismuth probes they confirmed the results of Fig. 19-5. But with an especially thin slit, namely, 1.2×10^{-2} cm, in a spherical single crystal of tin 3.9 cm in diameter, they found large irregular fluctuations of the field strength, corresponding to the irregular distribution of normal and superconducting domains.

Figure 19-8 shows the results at 3° K, corresponding to a critical value of the field at 97 oersteds. Curve A shows the field distribution along a diameter when the external field H^0 is less than $(2/3)H_c$, i. e., 65 oersteds. The sphere, being superconducting as a whole, completely excludes the field, but there is already a trace of the field if H^0 exceeds $(2/3)H_c$ by only 2 oersteds (curve B). The maxima showing this effect increase in number with increasing H^0 . At $H^0 = 94$ oersteds (curve G) the field has penetrated the sphere almost completely, and at $H^0 = 110$ oersteds it has the same value inside as outside the sphere.

The authors emphasize the fact that it is impossible to reproduce the curves exactly, although their general character remains the same with repeated experiments. The irregularity of the intermediate state is demonstrated by the accidental form of the field distribution.

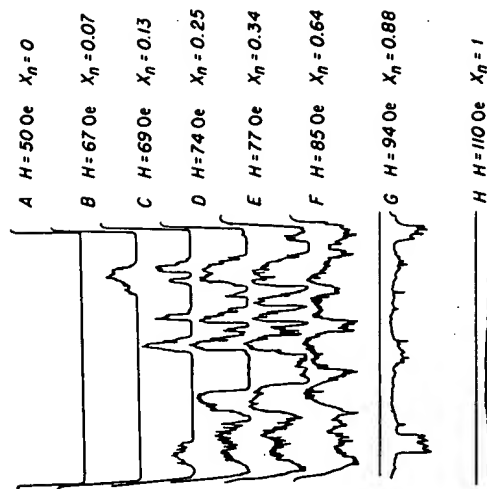


Fig. 19-8. Magnetic field strength as function of position within a narrow equatorial slit in a single crystal tin sphere measured by movable bismuth probes, according to Meshkovski and Shalnikov.

⁷A. Meshkovski and A. Shalnikov, *J. Physics (U.S.S.R.)* **11** (1947).

(b) We shall not change any of the fundamental equations enumerated in Chap. 3 except the relation between supercurrent density \mathbf{i}^s and the supercurrent momentum \mathbf{G} , i. e., we abandon eqs. VIII and VIII a, but retain all the other equations indicated by roman numerals. The new relation will be left open to a considerable extent, it being required only that it shall be uniquely reversible and go over to the linear relation VIII (or VIII a) for sufficiently weak currents; that a change of sign of \mathbf{i}^s shall cause a change of sign of \mathbf{G} , and the angle between \mathbf{i}^s and \mathbf{G} shall always be acute so that

$$(\mathbf{i}^s \cdot \mathbf{G}) > 0 \quad (20-1)$$

For a given direction of \mathbf{i}^s the absolute value of \mathbf{G} and the absolute value of \mathbf{i}^s increase simultaneously.

The most important restriction, however, arises from the energy principle. Equation 5-4 can be taken over immediately, and by eq. IX we can put in that equation

$$(\mathbf{E} \cdot \mathbf{i}^s) = \left(\mathbf{i}^s \cdot \frac{\partial \mathbf{G}}{\partial t} \right) \quad (20-2)$$

We require that the integral

$$F^s \equiv \int \left(\mathbf{i}^s \cdot \frac{\partial \mathbf{G}}{\partial t} \right) dt \quad (20-3)$$

shall depend only on the final supercurrent density when the latter is zero at the beginning, being independent of the intermediate states through which it has passed. Owing to the assumption of unique reversibility of the relation between \mathbf{i}^s and \mathbf{G} we can also state that F^s depends only on the momentarily existing supercurrent momentum \mathbf{G} , or alternatively, that the integral

$$F^s = \int_0^G (\mathbf{i} \cdot d\mathbf{g}) \quad (20-4)^3$$

shall be independent of the path of integration in \mathbf{G}_a space. Otherwise the theory would lead to energy transformations within the superconductor contradictory to observation. Under these conditions eq. 20-4 becomes the definition of the density of free energy F^s associated with the supercurrent. The mathematical expression for these conditions is:

$$\frac{\partial i_a^s}{\partial G_\beta} - \frac{\partial i_\beta^s}{\partial G_a} = 0 \quad (a, \beta = 1, 2, 3) \quad (20-5)$$

This ensures that the integral appearing in the equation

³ In the integrand it is to be understood that \mathbf{l} and \mathbf{g} are variables of integration that assume the values \mathbf{i}^s and \mathbf{G} at the upper limit. The relation between \mathbf{l} and \mathbf{g} is naturally the same as between \mathbf{i}^s and \mathbf{G} .

CHAPTER 20

A Nonlinear Extension of the Theory¹

(a) According to Chap. 17 the breakdown of superconductivity becomes inevitable for thermodynamic reasons as soon as the energy density $\frac{1}{2}(\mathbf{i}^s \cdot \mathbf{G})$ reaches the critical value $f(N - f_s)/V$ at any point of the surface, the transformation into the normally conducting phase starting at that point (eq. 17-4). For a "thick" superconductor, we can, according to eq. 7-37 put $\frac{1}{2}(\mathbf{i}^s \cdot \mathbf{G}) = \frac{1}{2}H_0^2$ and this leads to the critical value of the magnetic field strength given by eq. 17-5. However, the atomic theory of superconductivity recently developed by Heisenberg² leads to the idea of a maximum density of the supercurrent that cannot be exceeded because of quantum theoretical restrictions. The question arises: Is this a new stability condition for the superconducting phase? Is the breakdown of superconductivity possible from within, and how is this related with thermodynamics?

The maximum current density i_m like the critical magnetic field strength H_c must be a function of temperature. They are both zero at the transition temperature T_c . Also i_m is zero at absolute zero temperature and has a maximum, according to current estimates, in the neighborhood of $\frac{1}{2}T_c$. According to Chap. 1, Fig. 1-4, the critical field H_c increases continuously with decreasing temperature. This different behavior emphasizes the importance of the following question: If the maximum current density, and therefore for a wire of given thickness the maximum total current, decreases toward zero with decreasing temperature, how can the supercurrent produce the field strength at the surface required by thermodynamics for the breakdown of superconductivity?

There is no upper limit to the current density in the theory so far presented in this book. We shall make it possible to include such a maximum current by means of a nonlinear extension of the theory without sacrificing very many of its results. This step was also suggested by the fact that experimentalists have for some time doubted whether the penetration depth of a transverse field in a wire is actually independent of the field strength in the manner required for the theory of Chap. 9.*

¹ Compare the following references:

M. v. Laue, *Ann. Physik*, (6) 5, 197, 1949.

W. Heisenberg, (a) *Z. Naturforsch.*, 2a, 185 (1947); (b) *Z. Naturforsch.*, 8a, 65 (1948);

(b) *Göttingen Nachr. Math.-Physik. Klasse*, 1947, p. 23; (d) *Ann. Physik*, 8, 289 (1948)

H. Koppe, (a) *Z. Naturforsch.*, 4a, 79 (1949); (b) *Ergeb. exakt. Naturw.*, 28, 283, (1950).

² See Heisenberg reference in footnote 1.

* Compare A. B. Pippard, *Proc. Roy. Soc. A* 208, 195, 210, (1950).

$$F_s = (\mathbf{i}^s \cdot \mathbf{G}) - \int_0^{\mathbf{i}^s} (\mathbf{g} \cdot d\mathbf{i}) \quad (20-6)$$

shall be independent of the path of integration in \mathbf{i}_a^s space and leads to conditions equivalent with eq. 20-5, namely,

$$\frac{\partial G_a}{\partial \mathbf{i}^s} - \frac{\partial G_\beta}{\partial \mathbf{i}_\beta^s} = 0 \quad (a, \beta = 1, 2, 3) \quad (20-7)$$

From eq. 20-1 it then follows that

$$F_s > 0 \quad (20-8)$$

Equation 20-4 may now be integrated in \mathbf{G}_a space along the straight line that connects the origin (zero \mathbf{G}) with the end of the vector \mathbf{G} . On this line increments $d\mathbf{G}_a$ are proportional to \mathbf{G}_a and have the same sign, so that $(\mathbf{i} \cdot d\mathbf{g}) > 0$ along the whole path. The same argument applied to the \mathbf{i}_a^s space proves that the integral in eq. 20-6 is positive. It therefore follows that

$$F_s < (\mathbf{i}^s \cdot \mathbf{G}) \quad (20-9)$$

The surfaces $F_s = \text{constant}$ will be closed shells in both \mathbf{G}_a space and in \mathbf{i}_a^s space. They will have the same symmetry as that of the crystal class about the origin as center. As long as the linear approximation VIII holds, eq. 20-7 goes over into the symmetry condition $\lambda_{a\beta} = \lambda_{\beta a}$, and the surfaces are ellipsoids or spheres for the cubic system. In the general case they have less simple forms, and in general \mathbf{i}^s and \mathbf{G} are different in direction even for the cubic system. If \mathbf{i}^s happens to coincide in direction with an axis of rotation, \mathbf{G} must do the same because of the uniqueness of their relationship, and of course this is true for any crystal class.

The possibility cannot be excluded that there exists a surface in \mathbf{i}_a^s space, at a finite distance from the origin, corresponding to infinite free energy $F_s = \infty$. The vector \mathbf{i}^s could then never grow beyond that surface, and there would exist a maximum current density dependent on direction. At such a surface \mathbf{G} would also become infinite, for otherwise F_s must remain finite by eq. 20-9. Under these circumstances the energy principle (compare eq. 5-5) takes the form

$$\frac{\partial}{\partial t} \left\{ \frac{1}{2} \mathbf{E}^2 + \frac{1}{2} \mathbf{H}^2 + F_s \right\} + (\mathbf{i}^0 \cdot \mathbf{E}) + c \operatorname{div} [\mathbf{E} \times \mathbf{H}] = 0 \quad (20-10)$$

Just as in Chap. 5, we can conclude from this that space charges in a superconductor compensate each other in a short time, or move to the surface until the total density $\rho = \rho^0 + \rho^s$ vanishes. We do not learn anything from this theory about ρ^s itself.

By integrating the integral in eq. 20-6 along the same straight line in \mathbf{i}_a^s space one can put

$$(\mathbf{g} \cdot d\mathbf{i}) = \left[\frac{(\mathbf{g} \cdot \mathbf{i})}{|\mathbf{i}|} \right] d|\mathbf{i}|$$

For the linear theory the component $(\mathbf{g} \cdot \mathbf{i})/|\mathbf{i}|$ of the vector \mathbf{g} in the direction \mathbf{i} becomes proportional to $|\mathbf{i}|$, as shown by the straight line in Fig. 20-1. We then find (in agreement with eq. 5-6)

$$\int_0^{\mathbf{i}^s} (\mathbf{g} \cdot d\mathbf{i}) = \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F_s = \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s)$$

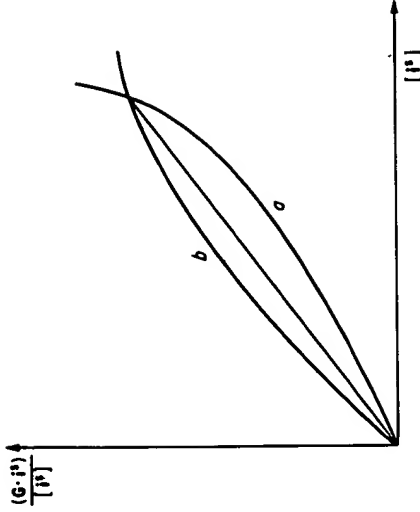


Fig. 20-1. Schematic representation of the types of nonlinear relations between supercurrent momentum \mathbf{G} and supercurrent density \mathbf{i}^s . Abscissa: magnitude of the supercurrent \mathbf{i}^s . Ordinate: component of supercurrent momentum in direction of the supercurrent.

In the nonlinear theory the relation between $(\mathbf{g} \cdot \mathbf{i})/|\mathbf{i}|$ and $|\mathbf{i}|$ can be represented for example by a curve of the type a in Fig. 20-1. Then clearly

$$\int_0^{\mathbf{i}^s} (\mathbf{g} \cdot d\mathbf{i}) < \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F_s > \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s) \quad (20-11)$$

while for a curve of the type b in Fig. 20-1 we would have

$$\int_0^{\mathbf{i}^s} (\mathbf{g} \cdot d\mathbf{i}) > \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s), \quad F_s < \frac{1}{2} (\mathbf{G} \cdot \mathbf{i}^s) \quad (20-12)$$

The existence of a maximum current density corresponds to the case a because here \mathbf{G} increases more rapidly than proportional to \mathbf{i}^s .

(c) We now have to find out to what extent the results of the linear theory still apply, and we start with the Meissner effect.⁴

⁴The equation 7-4 is still valid because in proving it the relation between \mathbf{G} and \mathbf{i}^s is never used. However we cannot take over the proof of the uniqueness theorem following eq. 7-4 because the difference field between two possible fields is no longer itself a possible field; i. e., one that satisfies the fundamental equations.

Let us first consider, as in Chap. 7, the stationary state with all field quantities depending only on x_3 . Because of $\text{div } \mathbf{i} = 0$ and $\text{div } \mathbf{H} = 0$, we get as before $i_3 = 0$, $H_3 = 0$, but G_3 is generally different from zero. Equation X, under this assumption, yields

$$-\frac{dG_1}{dx_3} = H_2, \quad c \frac{dG_2}{dx_3} = H_1 \quad (20-13)$$

whereas from II,

$$-i_1 = c \frac{dH_2}{dx_3}, \quad i_2 = c \frac{dH_1}{dx_3} \quad (20-14)$$

Elimination of \mathbf{H} leads to the partial differential equations

$$c^2 \frac{d^2 G_1}{dx_3^2} = i_1^2, \quad c^2 \frac{d^2 G_2}{dx_3^2} = i_2^2 \quad (20-15)$$

in which G_1 and G_2 have to be regarded as functions of i_1 and i_2 respectively. These equations replace the former differential equation $\Delta u - \beta^2 u = 0$. Taking the product of the first of these with G_1 and the second with G_2 and adding the results we obtain

$$G_1 \frac{d^2 G_1}{dx_3^2} + G_2 \frac{d^2 G_2}{dx_3^2} = \frac{1}{c^2} (\mathbf{i} \cdot \mathbf{G})$$

and by eq. 20-13:

$$\begin{aligned} \frac{d^2}{dx_3^2} (G_1^2 + G_2^2) &= \frac{2 (\mathbf{i} \cdot \mathbf{G})}{c^2} + \left(\frac{dG_1}{dx_3} \right)^2 + \left(\frac{dG_2}{dx_3} \right)^2 \\ &= \frac{2 (\mathbf{i} \cdot \mathbf{G})}{c^2} + \frac{H^2}{c^2} \end{aligned} \quad (20-16)$$

On the other hand, if we multiply the left-hand equations of 20-13 and 20-14 together, and also the right-hand equations, and add the results, we find, by using eq. 20-4 that

$$\frac{dF_3}{dx_3} = \frac{1}{2} \frac{d(H^2)}{dx_3} \quad (20-17)$$

or, by introducing an arbitrary integration constant C ,

$$F_3 = \frac{1}{2} H^2 - C \quad (20-18)$$

Using eqs. 20-18 and 20-15 gives

$$\frac{d^2}{dx_3^2} (G_1^2 + G_2^2) = \frac{2}{c^2} [(\mathbf{i} \cdot \mathbf{G}) + F_3 + C] \quad (20-19)$$

Here $(\mathbf{i} \cdot \mathbf{G})$ and F_3 are to be regarded as known functions of i_1 and i_2 just as are G_1 and G_2 .

In order to discuss eq. 20-19, we now write z for x_3 and put $G_1^2 + G_2^2 \equiv u(z)$. According to eq. 20-16 $u'' > 0$, so the curve of $u(z)$ is everywhere concave upwards. To within the linear approximation $(\mathbf{i} \cdot \mathbf{G})$ as well as F_3 are proportional to $(G_1^2 + G_2^2)$, the proportionality factor depending on the ratio G_1/G_2 . In any case, on this approximation eq. 20-19 assumes the form

$$u'' = A^2 (u + C')$$

where A is a constant and C' another constant proportional to C . The solution in terms of another integration constant B is

$$u + C' = B \exp [\pm A (z - z_0)]$$

We use the lower sign and choose $C = 0$, therefore also $C' = 0$. Then u and therefore also G_1 and G_2 approach zero with increasing z . By eqs. 20-13 and 20-14 i_1 and H decrease exponentially with increasing z , in agreement with Chap. 7. However, $(G_1^2 + G_2^2)$ increases in the negative z direction because of the positive u'' , finally without limit. It depends upon the relation between i_1 and G whether u increases without limit at a finite z or only at infinite z . In any case we can, by choosing a suitable value for z_0 , arrange for $H^2 = c^2 [(dG_1/dx_3)^2 + (dG_2/dx_3)^2]$ to have any prescribed value H^2 at $z = x_3 = 0$. To obtain also a prescribed direction for \mathbf{H} at the origin we must also be free to choose the ratio G_1/G_2 at any point appropriately.

Let the superconductor occupy the half space $x_3 > 0$ as in Chap. 7, while a homogeneous magnetic field \mathbf{H}^0 exists where $x_3 < 0$. Then the solutions just discussed will yield the Meissner effect, i. e., the restriction of the magnetic field in the superconductor to a protecting layer close under the surface.

For a plane parallel plate of finite thickness, C differs from zero. Indeed $C < 0$ if a current is passed through the plate without producing an additional magnetic field. Then $\mathbf{H} = 0$ exactly at the center of the plate, by symmetry, but i_1 and with it F_3 are different from zero. If instead we prescribe that the magnetic field \mathbf{H}^0 shall be the same at the two surfaces without passing a current through it, then $i_1 = 0$ but \mathbf{H} differs from zero and therefore $C > 0$ at the middle.⁵

⁵H. Koppe (see footnote 1) integrated the differential equation under the arbitrary assumption that

$$G = \frac{\lambda i_1}{\sqrt{1 - i_1^2/i_m^2}}$$

His result is represented in Fig. 20-2, which shows the field distribution in the superconducting half of space, $z > 0$. In this figure

$$i = \frac{|i_1|}{i_m} \quad h = \frac{H}{\sqrt{\lambda} i_m} \quad w = \frac{F_3}{\lambda i_m^2}$$

the unit for x_3 is $\exp \sqrt{\lambda}$. The boundary surface of the superconductor has to be so chosen that it coincides with the prescribed value of H^0 . If this value is comparatively small, the boundary lies fairly far to the left in the diagram and the field quantities decrease exponentially with increasing x_3 . If H^0 is relatively large, the boundary lies far to the right and the current density in the protecting layer is not much less than i_m over a wide region.

(d) In a cylinder carrying a current (Chap. 8) the situation becomes rather complicated unless the direction of the current coincides with a crystallographic axis of rotation, so that, by section (b), the vectors \mathbf{G} and \mathbf{i} are parallel. In this case we can use simply the magnitudes G and i .

Introducing cylindrical coordinates as in Chap. 8, G and i become functions of the radius vector only. The same is true of the component of the magnetic field H_θ in the θ direction. Equation X then yields,

$$c \frac{dG}{dr} = H_\theta \quad (20-20)$$

and from eq. II, (compare eq. 8-1)

$$i^2 = \frac{c}{r} \frac{d(r H_\theta)}{dr} \quad (20-21)$$

We proceed as in section (c). Eliminate \mathbf{H} and multiply the last two equations, and we then obtain

$$\frac{d}{dr} \left(r \frac{dG^2}{dr} \right) = \frac{2r}{c^2} (G i^2 + H_\theta^2) \quad (20-22)$$

i. e.,

$$r \frac{dG^2}{dr} = \frac{2}{c} \int_0^r r (G i^2 + H_\theta^2) dr$$

and after integration

$$F^2 = \frac{1}{2} H_\theta^2 + \int_0^r \frac{H_\theta^2}{r} dr + F_0^2 \quad (20-23)$$

The integration constant F_0^2 represents the energy density at the axis $r = 0$. According to eq. 20-22, $dG/dr > 0$, and this represents the Meissner effect.

Apply eq. 20-23 at the surface of the wire ($r = R$) where the field is H_0 . If R is large compared with a suitably defined penetration depth d , then the integral is at most of the order of magnitude $(H_0)^2 d/R$, and therefore small compared with $\frac{1}{2} (H_0)^2$. The same is true of F^2 . Consequently just as in eq. 20-18 where $C = 0$ for the "thick" superconductor,

$$F^2 = \frac{1}{2} (H_0)^2 \quad (20-24)$$

However, it is possible for $F^2 \gg \frac{1}{2} (H_0)^2$, if $F_0^2 \gg \frac{1}{2} H_\theta^2$, i. e., if the current is more or less uniformly distributed over the cross section of the cylinder.

(e) London's theorems concerning persistent currents (eqs. 12-11 and 12-13) remain unchanged. The proof of these equations does not use any relation between \mathbf{G} and \mathbf{i} . Likewise eq. 12-21 is still valid; the left-hand side is still positive for any really existing field even though it no longer represents the total free energy of the field. Thus on the nonlinear theory there still exist no magnetic fields that are not produced by one of the three following causes: annular currents in a superconductor, ohmic currents in

a normal conductor, and permanent magnetism. The proof that these causes determine the field uniquely cannot be given in the same way as in Chap. 12, because now the difference field is no longer a possible field as it was in the linear theory.

(f) Sections (c) to (e) show how little the nonlinear theory differs from the linear one for stationary fields. It is difficult to decide between then on the basis of experimental evidence at present available. The decisive question is whether on the nonlinear theory there also exists a stress tensor Θ depending on the supercurrent density as in Chap. 13 and exerting a volume force on a homogeneous superconductor that exactly cancels the force due to the Maxwell stress tensor. The fact that the resistance vanishes demands this unequivocally.

We now proceed to prove the impulse theorem 13-10 for the nonlinear theory. The force equation

$$\Theta_{\alpha\beta} = i_\beta^s G_\alpha - \delta_{\alpha\beta} F^s \quad (20-25)$$

provides the required proof, because actually it does not differ from eq. 13-1 if we write $P = \mathbf{i}$, $Q = \mathbf{G}$, because then $F^s = \frac{1}{2} \sum_\alpha i_\alpha^s G_\alpha$. The proof follows the earlier calculation of $\text{div } \Theta$. The x_1 component of this vector is defined in eq. 13-3, and we have to put

$$\Theta_{11} = i_1^s G_1 - F^s, \quad \Theta_{12} = i_2^s G_1, \quad \Theta_{13} = i_3^s G_1 \quad (20-26)$$

The differential coefficient $\partial F^s / \partial x_1$ appears in the result.

F^s depends both on \mathbf{i} and on certain parameters p_n which are present also in the relation between \mathbf{G} and \mathbf{i} . The p_n 's are functions of the temperature and differ from substance to substance. Whenever the superconductor is inhomogeneous, whether due to temperature differences or to differences in chemical composition (as in alloys at soldered boundaries), the p_n 's are functions of the coordinates x . From eq. 20-4 it therefore follows that

$$\frac{\partial F^s}{\partial x_1} = \sum_\alpha i_\alpha^s \frac{\partial G_\alpha}{\partial x_1} + \sum_{n,\gamma} \frac{\partial p_n}{\partial x_1} \int_0^G \left(\frac{\partial i_\gamma}{\partial p_n} \right) dg_\gamma$$

The suffix g indicates differentiation at constant g . Using eq. 20-26 the calculation yields

$$\text{div}_1 \Theta = \sum_{n=1}^{10} B_n$$

where

$$B_1 = i_1^s \frac{\partial G_1}{\partial x_1}, \quad B_2 = G_1 \frac{\partial i_1^s}{\partial x_1}, \quad B_3 = -i_1^s \frac{\partial G_1}{\partial x_1}$$

$$B_4 = -i_2^s \frac{\partial G_2}{\partial x_1}, \quad B_5 = -i_3^s \frac{\partial G_3}{\partial x_1}$$

$$B_6 = - \sum_{n,\gamma} \frac{\partial p_n}{\partial x_1} \int_0^G \left(\frac{\partial i_\gamma}{\partial p_n} \right) dg_\gamma$$

$$B_7 = i_2^s \frac{\partial G_1}{\partial x_2}, \quad B_8 = G_1 \frac{\partial i_2^s}{\partial x_2}$$

$$B_9 = i_3^s \frac{\partial G_1}{\partial x_3}, \quad B_{10} = G_1 \frac{\partial i_3^s}{\partial x_3}$$

One sees at once that

$$B_1 + B_3 = 0, \quad B_2 + B_8 + B_{10} = G_1 \operatorname{div} \mathbf{i}^s$$

$$B_4 + B_7 = -i_2^s \operatorname{curl}_3 G, \quad B_5 + B_9 = i_3^s \operatorname{curl}_2 G$$

Therefore

$$\operatorname{div} \Theta = G \operatorname{div} \mathbf{i}^s - [\mathbf{i}^s \times \operatorname{curl} G] - \sum_{n,\gamma} \operatorname{grad} p_n \int_0^{\mathbf{i}^s} \left(\frac{\partial i_\gamma}{\partial p_n} \right) d\mathbf{g}_\gamma \quad (20-27)$$

This agrees with eq. 13-5 apart from the form of the term representing inhomogeneity. The argument following eq. 13-5 in Chap. 13 does not make use of the relation between G and \mathbf{i}^s , and therefore applies in the present case and leads to the impulse theorem (compare eq. 13-10)

$$-\operatorname{div} [T(\mathbf{E}) + T(\mathbf{H}) + \Theta] = \rho^0 \mathbf{E} + \frac{1}{c} [\mathbf{i}^0 \times \mathbf{H}] +$$

$$+ \sum_{n,\gamma} \operatorname{grad} p_n \int_0^G \left(\frac{\partial i_\gamma}{\partial p_n} \right) d\mathbf{g}_\gamma + \frac{\partial}{\partial t} \left[\frac{1}{c} [\mathbf{E} \times \mathbf{H}] + \rho^s \mathbf{G} \right] \quad (20-28)^e$$

The whole discussion that follows the impulse theorem concerning the volume forces and the torque due to asymmetry of the tensor

$$\Theta_{23} - \Theta_{32} = [G \times \mathbf{i}^s]_1, \text{ etc.}$$

remains valid here. The new fact that arises is that this asymmetry appears now even in cubic crystal superconductors, at least when we go beyond the region where the linear approximation is sufficient.

(g) Differences from the linear theory appear when we discuss the individual stress components. If we choose the x_1 direction parallel to \mathbf{i}^s

^eFrom eq. 20-8 it follows by differentiation with respect to p_n at constant \mathbf{i}^s and G that

$$\sum_{\gamma} \int_0^G \left(\frac{\partial i_\gamma}{\partial p_n} \right) d\mathbf{g}_\gamma = - \sum_{\gamma} \int_0^{\mathbf{i}^s} \left(\frac{\partial \mathbf{g}_\gamma}{\partial p_n} \right) d\mathbf{i}_\gamma$$

The third term on the right-hand side of eq. 20-28 can therefore also be written in the alternative form given by M. von Laue (footnote 1)

$$- \sum_{n,\gamma} \operatorname{grad} p_n \int_0^{\mathbf{i}^s} \left(\frac{\partial \mathbf{g}_\gamma}{\partial p_n} \right) d\mathbf{i}_\gamma$$

at some point in space, four of the nine components of Θ vanish there and the others have the values:

$$\Theta_{11} = (\mathbf{i}^s \cdot G) - F^s, \quad \Theta_{22} = \Theta_{33} = -F^s, \quad \Theta_{21} = i_1^s G_2, \quad \Theta_{31} = i_1^s G_3 \quad (20-29)$$

The components Θ_{21} and Θ_{31} also vanish if \mathbf{i}^s and G are parallel, and then the current line is, just as before, one of the principal axes of rotational symmetry of the tensor Θ . A tension F^s acts perpendicular to the current line, and a pressure acts along it because $\Theta_{22} = \Theta_{33} < 0$ while $\Theta_{11} > 0$ according to eqs. 20-8 and 20-9. However, the pressure is no longer equal to the tension, but, by eq. 20-11 is smaller than the tension when G and \mathbf{i}^s are related as in curve *a* of Fig. 20-1, and greater for the curve *b*.

In any case, according to eq. 20-29 a supercurrent flowing parallel to the surface of a superconductor must exert a force that has both a tangential and a normal component across the surface into the interior amounting to F^s per unit area. The work done by this field upon a surface element $d\sigma$ displaced a distance ∂u toward the interior of the superconductor amounts therefore to $F^s d\sigma \partial u$. Therefore the thermodynamic equilibrium condition at the boundary between normally and superconducting phases of the same substance is (compare Chap. 17)

$$F^s = \frac{(f_N - f_S)}{V} \quad (20-30)$$

while at the free (outside) surface of the superconductor

$$F^s \leq \frac{(f_N - f_S)}{V} \quad (20-31)$$

In so far as $F^s = \frac{1}{2} (\mathbf{i}^s \cdot G)$ this agrees with eqs. 17-3 and 17-4.

For very thick specimens we can write $\frac{1}{2} (H^0)^2$ for F^s , by eq. 20-24 and so get exactly the form 17-6 and 17-7 for the equilibrium conditions. As the whole of the thermodynamics of this transition can be derived from this condition, according to Chap. 17, it remains unaffected by altering the electrostatics in the above manner. For a plate of finite thickness however $C > 0$ in eq. 20-18 by section (c). If the magnetic field on both sides of the plate has the critical value H_c , then by eq. 20-31, F^s at the boundary has a lower value than the critical one. We then have to increase the external field to bring F^s to its critical value, i. e., for thin superconductors the critical field strength is greater than for thick ones. This agrees qualitatively with the results of Chap. 18, which however no longer hold quantitatively in the nonlinear theory. The results depend on the relation between G and \mathbf{i}^s so that it should in principle be possible to derive conclusions about this relation from experimental data on the dependency of the critical magnetic field on the thickness of the plate.

(h) We now turn to the case where there does exist a maximum current density i_m , i. e., the family of surfaces in \mathbf{i}^s space converge upon a finite surface on which F^s becomes infinite.

We consider first the superconductor of section (c), occupying half of space. If i_1^s at the surface is only a little below i_m , while $i_2^s = 0$ (this can

always be done by choosing the appropriate direction for the coordinates x_1 and x_2), then by eq. 20-15 G_1 decreases with increasing x_3 , but not as in Chap. 7 (exponentially in one way or another) but much more slowly, approximately in the form of a parabola. By eq. 20-13 H_0 thus becomes a linear function of x_3 (compare Fig. 20-2), and this causes the protecting layer to become thicker than on the linear theory. As a matter of fact, to completely shield the field H^0 the Maxwell theory would require a total surface current cH^0 , and this, when the current density is limited, would have to be distributed over a thicker protecting layer. The penetration depth therefore becomes greater than in the linear theory and dependent on H^0 .

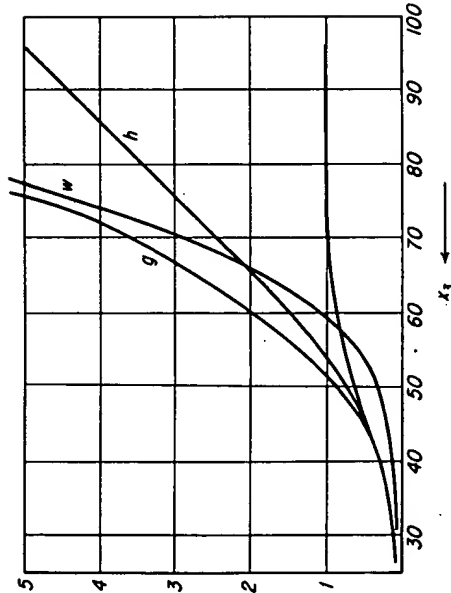


Fig. 20-2. Field distribution in the superconductor filling half space $x_3 > 0$ according to Koppe (see footnote 1, Chapter 20). Abscissa: x_3 in units of $\exp \sqrt{\lambda}$.

Ordinate:

$$i = |j|/i_m, \quad h = H/\sqrt{\lambda} i_m, \\ g = G/c\sqrt{\lambda} i_m, \quad w = F^2/\lambda i_m^2$$

When a cylinder of radius R (section d) carries a current, the field H^0 at the surface is definitely less than the value $R i_m/2c$ that would exist if the current density were equal to i_m over the whole cross section. In spite of this limitation on H^0 , F^2 can by eq. 20-23 attain any value at the surface, including the critical value given by eq. 20-31, so long as F_0^2 already has approximately this value, i. e., so long as the current is somewhat uniformly distributed over the cross section.⁷ But F^2 is nowhere so great as it is at the surface, and it is also there that the greatest danger to the superconductivity lies, and it is also there that the breakdown starts as soon as F^2 reaches the critical value. This is true no matter how great the critical value may

⁷The same conclusion can be drawn from eq. 20-18 with $C < 0$.

be or how small the maximum current density. The upper limit of the current density is therefore not a new condition for the stability of the supercurrent; the thermodynamic relations 20-30 or 20-31 are still necessary and sufficient.⁸

(†) Although the nonlinear theory agrees at least qualitatively, and in many important problems even quantitatively, with the linear theory for all stationary fields, in discussing oscillatory fields the linear theory can only be regarded as an approximation for oscillations of sufficiently small amplitude.

APPENDIX

Proof of Equation 14-8

If matter undergoes an arbitrary but continuous displacement ∂u then the change dP of an arbitrary vector P at a moving (material) point is related with the change ∂P at a given point in space through the equation

$$dP_a = \partial P_a + \sum_{\gamma} \partial u_{\gamma} \frac{\partial P_a}{\partial x_{\gamma}} + \frac{1}{2} [P \times \text{curl } \partial u]_a$$

Therefore

$$d(P_a P_{\beta}) = \partial(P_a P_{\beta}) + P_{\alpha} \left\{ \sum_{\gamma} \partial u_{\gamma} \frac{\partial P_{\beta}}{\partial x_{\gamma}} + \frac{1}{2} [P \times \text{curl } \partial u]_{\beta} \right\} \\ + P_{\beta} \left\{ \sum_{\gamma} \partial u_{\gamma} \frac{\partial P_a}{\partial x_{\gamma}} + \frac{1}{2} [P \times \text{curl } \partial u]_{\alpha} \right\} \quad (a)$$

$P_a P_{\beta}$ are the components of a symmetrical tensor, say $t_{a\beta}$. For the most general formulation of the symmetrical tensor we have to combine three noncoplanar vectors P, Q, R as follows:

$$P_a P_{\beta} + Q_a Q_{\beta} + R_a R_{\beta}$$

The two additional terms do not alter the form of the transformation $\partial t_{a\beta}$ into $\partial t_{a\beta}$, so we confine ourselves to the definition

$$t_{a\beta} = P_a P_{\beta}$$

Transcribing (a) we then have

$$d t_{11} = \partial t_{11} + \sum_{\gamma} \partial u_{\gamma} \frac{\partial t_{11}}{\partial x_{\gamma}} + \frac{1}{2} (t_{12} \text{curl}_3 \partial u - t_{13} \text{curl}_2 \partial u)$$

⁸According to the above considerations (see M. von Laue, footnote 1), Silsbee's hypothesis [compare Chap. 1 (e)] is now valid only for sufficiently "thick" superconductors.

$$dt_{23} = \partial t_{23} + \sum_{\gamma} \partial u_{\gamma} \frac{\partial t_{23}}{\partial x_{\gamma}} + \frac{1}{2} \{ (t_{33} - t_{22}) \text{curl}_1 \partial u + t_{12} \text{curl}_2 \partial u - t_{13} \text{curl}_3 \partial u \}$$

etc.

Just as in Chap. 14 we now assume that all the $dt_{\alpha\beta}$'s are zero so that

$$\partial t_{11} = - \sum_{\gamma} \partial u_{\gamma} \frac{\partial t_{11}}{\partial x_{\gamma}} - \frac{1}{2} (t_{13} \text{curl}_2 \partial u - t_{12} \text{curl}_3 \partial u) \quad (b)$$

$$\partial t_{23} = - \sum_{\gamma} \partial u_{\gamma} \frac{\partial t_{23}}{\partial x_{\gamma}} + \frac{1}{2} \{ (t_{22} - t_{33}) \text{curl}_1 \partial u - t_{12} \text{curl}_2 \partial u + t_{13} \text{curl}_3 \partial u \}$$

Let Q be another arbitrary vector. In (b) collect all the terms with $\text{curl}_1 \partial u$, all those with $\text{curl}_2 \partial u$ and all those with $\text{curl}_3 \partial u$, and obtain

$$\begin{aligned} \frac{1}{2} \sum_{\alpha\beta\gamma} Q_{\alpha} Q_{\beta} \partial t_{\alpha\beta} &= \frac{1}{2} Q_1^2 \partial t_{11} + \dots + Q_2 Q_3 \partial t_{23} + \dots = \\ &- \frac{1}{2} \sum_{\alpha\beta\gamma} Q_{\alpha} Q_{\beta} \frac{\partial t_{\alpha\beta}}{\partial x_{\gamma}} \partial u_{\gamma} \\ &+ \frac{1}{2} \{ \text{curl}_1 \partial u [(Q_3^2 - Q_2^2) \partial t_{23} + Q_1 Q_3 t_{12} - Q_1 Q_2 t_{13} + Q_2 Q_3 (t_{22} - t_{33})] \\ &+ \text{curl}_2 \partial u [\text{a similar factor to the above}] \\ &+ \text{curl}_3 \partial u [\text{a similar factor to the above}] \} \end{aligned}$$

This equation can be simplified by introducing the following vector:

$$R_{\alpha} \equiv \sum_{\beta} t_{\alpha\beta} Q_{\beta}$$

We then obtain

$$\frac{1}{2} \sum_{\alpha\beta} Q_{\alpha} Q_{\beta} \partial t_{\alpha\beta} = - \frac{1}{2} \sum_{\alpha\beta} Q_{\alpha} Q_{\beta} (\partial u \cdot \nabla t_{\alpha\beta}) + \frac{1}{2} (\text{curl} \partial u \cdot [R \times Q]) \quad (c)$$

Finally writing i in place of Q , G for R and $\lambda_{\alpha\beta}$ for $t_{\alpha\beta}$ we confirm eq. 14-8.

INDEX

- | | |
|--------------------------------------|--|
| Acceleration theory, 18 | Magnetic field |
| Bessel equation, 35 | — critical value, 4, 6, 105, 112, 120, 126 |
| — functions, 36 | — at transition temperature, 108 |
| Cathode rays, 19, 20 | — temperature dependence, 5, 108 |
| Crystals, and superconduction, 15-17 | — thin superconductors, 27. |
| Debye's law, 110 | 112-120, 135 |
| Eddy currents, 102 | — distortion, 7, 112 |
| Electrons mean free path, 102, 103 | — circular cylinder, 55 |
| Energy, 20-22 | — sphere, 58 |
| — electric, 9 | — external, penetration of, 121 |
| — free, 22, 104; 106 | — in superconductors, 6-8, 30 |
| — density, 127-137 | — intensification factor, 112 |
| — temperature dependence, 106 | — moment, 70 |
| — magnetic, 9 | Maxwell equations, 13 |
| — total density, 21 | — from least action principle, 9, 10 |
| Entropy, 106, 107 | Maxwell-London theory, 12 |
| Equilibrium conditions, 105, 109 | Maxwell stresses, 75-84 |
| — stable, 71 | — and torque, 82, 84 |
| Extinction coefficient, 92 | — tensors of, 77 |
| Hankel function, 44 | Maxwell theory, 6 |
| Induction, coefficient, 12, 14 | Meissner effect, 7, 27, 30, 66, 80, 106. |
| — equations, 9, 11 | 129-132 |
| Kirchhoff's rule 8, 9 | — and skin effect, 94 |
| Lattice structure 4 | — — superconducting states, 107 |
| — and conducting phase, 103 | — disappearance of, 121 |
| Lines of force, for sphere, 60 | Momentum law, equation of, 78 |
| — thin cylinder, 52 | Multiply connected region, 62 |
| London's fundamental equations, 14 | Nernst theorem, 106, 108 |
| — relativistic form, 14 | Ohmic current, 106 |
| London stresses, 75-84, 118 | — distribution in superconductor, 72 |
| — and torque, 82 | — existence of, 94 |
| — surface divergence, 18 | Penetration depth, 3, 126 |
| — tension, 104 | — and alternating currents, 94-103 |
| | — — mean free path of electrons, 102, 10 |
| | — — non-linear theory, 136 |
| | — of magnetic field, 27 |
| | — increase, 67 |

- Penetration near transition temperature, 32
 - relation to flux of induction, 75
- Persistent current, 3, 10, 61—75, 132
 - energy, 73, 74, 91
 - in doubly connected body, 41, 49
 - — ring, 68
 - production, 70
- Potential, scalar and vector, 61
 - superconduction 63
 - — period of, 65, 67, 85
- Poynting sector, 21, 78, 96
- Refractive index, 92, 93
- Silsbee hypothesis, 6, 118
- Skin effect, 94—103
- Specific heat, 107, 108
 - of conduction electrons, 110
 - at transition temperature, 110
- Stress tensor, 76
 - and non-linear theory, 133
- Superconductivity
 - atomic theory, 126
 - breakdown, 105, 126
 - quenching, 7, 8, 112
 - — for thin specimen, 113
 - — — sphere, 121
 - permanent magnetism, 89, 106
- Superconductor, crystal systems, 2
 - current distribution, 11
 - displacement of current lines 72

- Superconductor field free state, 7, 103
 - homogeneous cubic, 26
 - inhomogeneous, 88
 - magnetic field, 4, 12
 - space charges, 19, 20, 128
 - thin—27—34
- Super current 3, 4
 - critical value of 6, 114, 115
 - in circular cylinder, 35
 - — elliptic cylinder, 53
 - — hollow cylinder, 44
 - — stationary field, 68
 - maximum density, 126—137
 - stability of 75, 76
 - velocity of 83, 84
- Supermomentum, 78
- Thermal expansion coefficient, 4
- Thermodynamics, 7, 103—112
 - equilibrium, 105, 119
- Transition from normal to superconductivity, 4
 - magnetic effect, 13
- Transition temperature
 - and magnetic field, 108
 - — penetration depth, 32
 - — resistance, 1, 2
 - — specific heat, 110
 - of metals, 2
- Uniqueness theorem, 25, 68

Attachment B

The Research Libraries of The New York Public Library /All Locations - Netscape

File Edit View Go Communicator Help

Back Forward Reload Home Search Netscape Print Security Stop

Instant Message Members WebMail Connections BizJournal SmartUpdate Marketplace RealPlayer

Bookmarks Location: <http://catnyp.nypl.org/search/q>

**CATNYP: The Online Catalog of The New York Public Library
The Research Libraries**

You searched: in

Limited to: Words in the TITLE "new directions in s"

Call # JSD 88-446
Author Rao, C. N. R. (Chintamani Nagesa Ramachandra), 1934-
Title **New directions in solid state chemistry : structure, synthesis, properties, reactions**
Imprint Cambridge [Cambridgeshire] ; New York : Cambridge University Press, 1986.

LOCATION	CALL #
Science & Business Lib	JSD 88-446

Location Science & Business Lib
Descript x, 516 p. : ill. ; 23 cm.
Series Cambridge solid state science series
Note Includes index.
Subject Solid state chemistry.
Add'l name Gopalakrishnan, J. (Jagannatha), 1939-

CATNYP: The Online Catalog of The New York Public Library

Document Done

Daniel P. Morris, Ph.D.
 Staff Counsel
 IBM Research
 IP Law Department Yorktown
 Tie line: 8-862-3217
 Phone: 914-945-3217
 Fax: 914-945-3281

Attachment C

Synthesis of cuprate superconductors*

C N R Rao, R Nagarajan and R Vijayaraghavan

Solid State and Structural Chemistry Unit and CSIR Centre of Excellence in Chemistry, Indian Institute of Science, Bangalore 560012, India

Received 28 August 1992, in final form 19 October 1992

Abstract. There has been unprecedented activity pertaining to the synthesis and characterization of superconducting cuprates in the last few years. A variety of synthetic strategies has been employed to prepare pure monophasic cuprates of different families with good superconducting properties. Besides the traditional ceramic method, other methods such as coprecipitation and precursor methods, the sol-gel method, the alkali flux method and the combustion method have been employed for the synthesis of cuprates. Depending on the requirements, varying conditions such as high oxygen or hydrostatic pressure and low oxygen fugacity are employed in the synthesis. In this review, we discuss the synthesis of the various types of cuprate superconductors and point out the advantages and disadvantages of the different methods. We have provided the necessary preparative details, presenting the crucial information in tabular form wherever necessary.

1. Introduction

Since the discovery of high- T_c superconductivity in the La-Ba-Cu-O system [1], a variety of cuprate superconductors with T_c s going up to 128 K have been synthesized and characterized [2, 3]. No other class of materials has been worked on so widely and intensely in recent years as have the cuprate superconductors. Several methods of synthesis have been employed for preparing the cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Specially noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distances in the solid state [5, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SHS) has also been employed. In this review, we will discuss the preparation of cuprate superconductors by the different methods, mentioning

the special features of each method and the conditions employed for the synthesis. In table 1, we give a list of the cuprate superconductors discussed in this review along with their structural parameters and approximate T_c values. Preparative conditions such as reaction temperature, oxygen pressure, hydrostatic pressure and annealing conditions are specified in the discussion and given in tabular form where necessary. It is hoped that this review will be found useful by practitioners of the subject as well as those freshly embarking on the synthesis of these materials.

2. Ceramic method

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the ceramic method [5]. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Platinum, silica or alumina containers are generally used for the synthesis of metal oxides. The starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature sufficiently long for the reaction to be completed. A knowledge of the phase diagram is useful in fixing the composition and conditions in such a synthesis.

The ceramic method generally requires relatively high temperatures (up to 2300 K) which are generally attained by resistance heating. Electric arc and skull

* Contribution No 874 from the Solid State and Structural Chemistry Unit.

Table 1. Structural parameters and approximate T_c values of cuprate superconductors.

	Cuprate	Structure	T_c (K) (max. value)
1	$\text{La}_2\text{CuO}_{4+x}$	Bmab; $a = 5.355, b = 5.401, c = 13.15 \text{ \AA}$	39
2	$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	I4/mmm; $a = 3.779, c = 13.23 \text{ \AA}$	35
3	$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	I4/mmm; $a = 3.825, c = 19.42 \text{ \AA}$	60
4	$\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821, b = 3.885, c = 11.676 \text{ \AA}$	93
5	$\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84, b = 3.87, c = 27.24 \text{ \AA}$	80
6	$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851, b = 3.869, c = 50.29 \text{ \AA}$	93
7	$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Amaa; $a = 5.362, b = 5.374, c = 24.622 \text{ \AA}$	10
8	$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A2aa; $a = 5.409, b = 5.420, c = 30.93 \text{ \AA}$	92
9	$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	A2aa; $a \sim 5.39, b \sim 5.40, c \sim 37 \text{ \AA}$	110
10	$\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888, c = 17.28 \text{ \AA}$	25
11	$\text{Tl}_2\text{Ba}_2\text{CuO}_6$	A2aa; $a = 5.468, b = 5.472, c = 23.238 \text{ \AA}$; I4/mmm; $a = 3.866, c = 23.239 \text{ \AA}$	92
12	$\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855, c = 29.318 \text{ \AA}$	119
13	$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	I4/mmm; $a = 3.85, c = 35.9 \text{ \AA}$	128
14	$\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83, c = 9.55 \text{ \AA}$	40
15	$\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a \sim 3.7, c \sim 9 \text{ \AA}$	40
16	$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738, c = 9.01 \text{ \AA}$	40
17	$\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856, c = 12.754 \text{ \AA}$	103
18	$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80, c = 12.05 \text{ \AA}$	90
19	$\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80, c = 12.10 \text{ \AA}$	90
20	$\text{TiCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	P4/mmm; $a = 3.853, c' = 15.913 \text{ \AA}$	110
21	$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	P4/mmm; $a = 3.81, c = 15.23 \text{ \AA}$	120
22	$\text{TiBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_8$	I4/mmm; $a \sim 3.8, c \sim 29.5 \text{ \AA}$	40
23	$\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	Cmmm; $a = 5.435, b = 5.463, c = 15.817 \text{ \AA}$	70
24	$\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_8$	P22 ₁ 2; $a = 5.333, b = 5.421, c = 12.609 \text{ \AA}$	32
25	$(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820, c = 11.826 \text{ \AA}$	50
26	$(\text{Pb}, \text{Cu})(\text{Sr}, \text{Eu})(\text{Eu}, \text{Ce})\text{Cu}_2\text{O}_7$	I4/mmm; $a = 3.837, c = 29.01 \text{ \AA}$	25
27	$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95, c = 12.07 \text{ \AA}$	30
28	$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902, c = 3.35 \text{ \AA}$	110
29	$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942, c = 3.393 \text{ \AA}$	40

techniques give temperatures up to 3300 K while high-power CO_2 lasers give temperatures up to 4300 K. The main disadvantages of the ceramic method are the following:

(i) The starting mixtures are inhomogeneous at the atomic level.

(ii) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by the diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and the reaction rate slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles.

(iii) There is no simple way of monitoring the progress of the reaction. It is by trial and error that one decides on the appropriate conditions required for the completion of the reaction. Because of this difficulty, with the ceramic method one often ends up with mixtures of reactants and products. Separation of the desired products from such mixtures is difficult, if not impossible.

(iv) Frequently it becomes difficult to obtain a compositionally homogeneous product even where the reaction proceeds nearly to completion.

Despite the above limitations, the ceramic method is widely used for the synthesis of a large variety of inorganic solids. In the case of the cuprate superconductors,

the ceramic method involves mixing and grinding the component oxides, carbonates or other salts, and heating the mixture, generally in pellet form, at the desired temperature. A common variation of the method is to heat a mixture of nitrates obtained by digesting the metal oxides/carbonates in concentrated HNO_3 and evaporating the solution to dryness. Heating is carried out in air or in an appropriate atmosphere, controlling the partial pressure of oxygen where necessary. In the case of thallium cuprates, because of the volatility and poisonous nature of the thallium oxide vapour, reactions are carried out in sealed tubes. In some of the earlier preparations, the thallium cuprates were synthesized in open furnaces. This is, however, not recommended. A successful synthesis by the ceramic method depends on several factors which include the nature of the starting materials (the choice of oxides, carbonates), the homogeneity of the mixture of powders, the rate of heating as well as the reaction temperature and duration.

2.1. La_2CuO_4 -related 214 cuprates

Synthesis of alkaline-earth-doped $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}$ and Ba) of K_2NiF_4 structure with superconducting transition temperatures up to 35 K is readily achieved by the ceramic method. Typically, the synthesis is carried out by reacting stoichiometric quantities of the oxides and/or carbonates around 1300 K in

air [1-9]. A few groups have annealed the samples in an oxygen atmosphere at 673 K after the sintering step [10]. Metal nitrates have also been used as the starting materials for the synthesis [11-13]. By starting with metal nitrates, one obtains a more homogeneous starting mixture, since the hydrated metal nitrates have low melting points leading to a uniform melt in the initial stage of the reaction. Furthermore, nitrates provide an oxidative atmosphere, which is required to obtain the necessary oxygen content.

Stoichiometric La_2CuO_4 is an antiferromagnetic insulator. La_2CuO_4 prepared under high oxygen pressures, however, shows superconductivity ($T_c \sim 35$ K) since the oxygen excess introduces holes just as the alkaline earth dopants [14-16]. $\text{La}_2\text{CuO}_{4+\delta}$ (δ up to 0.05) has been synthesized by annealing La_2CuO_4 under an oxygen pressure of 3 kbar at 870 K [14, 15] or 23 kbar at 1070 K [16]. Oxygen plasma has also been used to increase the oxygen content.

The next homologue of La_2CuO_4 containing two Cu-O layers, $\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$ ($T_c \sim 60$ K), has been synthesized by using high oxygen pressures [17]. The synthesis involves heating the sample at an oxygen pressure of around 20 bar at 1240 K. The material prepared at ambient oxygen pressures (in air) is an insulator. Several other high-oxygen-pressure preparations have been reported on the $n=2$ member of the $\text{La}_{n+1}\text{Cu}_n\text{O}_{2n+3}$ homologous series by making use of commercially available high-pressure furnaces [18, 19]. In table 2, we have summarized the preparative conditions for 214 and related cuprate superconductors.

2.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other 123 cuprates

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with the orthorhombic structure can be easily prepared by the ceramic method. Most of the investigations of the 123 compound, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been carried out on the materials prepared by reacting Y_2O_3 and CuO with BaCO_3 [20, 21]. It is noteworthy that Rao *et al* [21] obtained monophasic $\text{YBa}_2\text{Cu}_3\text{O}_7$ as the $x=1.0$ member of the $\text{Y}_{3-x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14}$ series. In the method employed for preparing $\text{YBa}_2\text{Cu}_3\text{O}_7$, stoichiometric quantities of high-purity Y_2O_3 , BaCO_3 and CuO are ground thoroughly and heated initially in powder form around 1223 K for a period of 24 h. Following the calcination step, the powder is ground, pelletized and sintered at the same temperature for another 24 h. Finally, annealing is carried out in an atmosphere of oxygen around 773 K for 24 h to obtain the orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase showing 90 K superconductivity. Oxygen annealing has to be carried out below the orthorhombic tetragonal transition temperature (~ 960 K); tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0.6 \leq \delta \leq 1.0$) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. Furthermore, CO_2 released from the decomposition of BaCO_3 can react with $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to form non-superconducting

phases at the grain boundaries. One way of avoiding the evolution of CO_2 during the synthesis is to use BaO_2 instead of BaCO_3 [22, 23]. Some of the impurities or side products in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ are BaCuO_2 , Y_2BaCuO_5 and $\text{Y}_2\text{Cu}_2\text{O}_5$ [24]. The ternary phase diagram given in figure 1 illustrates the complexities of this cuprate system.

Using BaO_2 as the starting material has two advantages. It has a lower decomposition temperature than BaCO_3 and the 123 compound is therefore formed at relatively low temperatures. BaO_2 acts as an internal oxygen source and the duration of annealing in an oxygen atmosphere is reduced to a considerable extent. Sharp superconducting transitions are observed in samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ made using BaO_2 . Slight excess of copper in the ceramic method is reported to give cuprates with sharper transitions [25]. Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is accomplished in a shorter period if one employs metal nitrates as the starting materials [13, 23]. In table 2, we present the conditions employed for preparing 123 cuprates by the ceramic method.

Other rare-earth cuprates of the 123 type, $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er}$ and Tm (all with T_c values around 90 K) have also been prepared by the ceramic method [26, 27]. Oxygen annealing of these cuprates should also be carried out below the orthorhombic-tetragonal transition temperature [3]: La, 754 K; Nd, 837 K; Gd, 915 K; Er, 973 K; Yb, 976 K etc. Nearly 30% of Y can be substituted by Ca in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, retaining the basic crystal structure [28]; the T_c decreases with the increase in calcium content. Both La and Sr can be substituted at the Ba site in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [29-31]. With La, monophasic products are obtained for $0 \leq x \leq 1.0$ in $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-\delta}$, the T_c decreasing with increase in x . In the case of Sr substitution, monophasic products are obtained for $0 \leq x \leq 1.25$ in $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$; high T_c is retained up to $x=1.0$. Ceramic methods have also been used to prepare $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$ solid solutions, where M generally stands for a transition element of the first series. In most

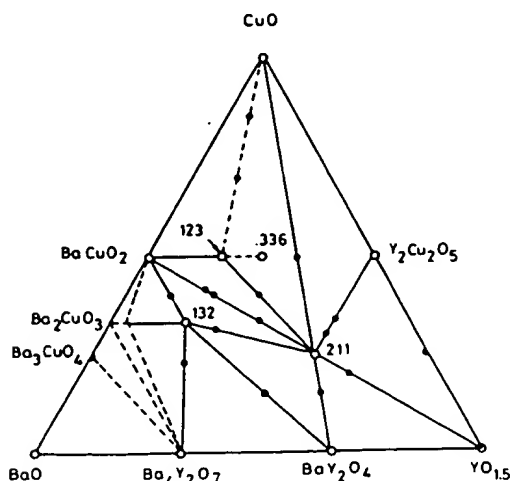


Figure 1. Phase diagram of the Y_2O_3 - BaO - CuO system at 1220 K (from [24]).

Table 2. Preparative conditions for the synthesis of 214, 123, 124 and 247 type cuprates by the ceramic method.

Compound	Starting materials	Preparative conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{La}_2\text{CuO}_{4+x}$	$\text{La}_2\text{O}_3, \text{CuO}$	1273 873	24 h 12–48 h	air O_2	3 kbar pressure	35	[15]
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	$\text{La}_2\text{O}_3, \text{Sr}/\text{BaCO}_3, \text{CuO}$	1393	36 h	O_2		40	[10]
$\text{La}_{1-x}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$	$\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Sr}/\text{Ba}(\text{NO}_3)_2, \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1273	20 h	air			
		973	16 h	O_2		32	[13]
	$\text{La}_2\text{C}_2\text{O}_4 \cdot 10\text{H}_2\text{O}, \text{Sr}(\text{NO}_3)_2, \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}, \text{CuO}$	1173	3 d	O_2			
		1198	3 d	O_2			
		1243	2 d	O_2		60	[17]
$\text{YBa}_2\text{Cu}_3\text{O}_7$ ^a	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1223 773	2 d 1 d	air	20 atm	88	[20]
$\text{YBa}_2\text{Cu}_4\text{O}_8$ ^b	$\text{Y}_2\text{O}_3, \text{BaO}_2, \text{CuO}$	1198	2 d	air		89	[22]
	$\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Ba}(\text{NO}_3)_2, \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1173	1 d	O_2			
		1223	1 h	air		90	[13]
		1313	—	O_2	400 bar	81	[34]
	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1023	1 d	O_2	124 major phase + BaCuO_2 impurity	77	[35]
	volumes of Na_2CO_3 or K_2CO_3	1073	3 d	O_2	124 major phase + BaCuO_2 + Y_2BaCuO_5	78	[36, 38]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO} + 0.2\text{M NaNO}_3$ or KNO_3 or Na_2O_2	1073	3 d	O_2	124 major phase + BaCuO_2 + Y_2BaCuO_5	78	[36]
	$\text{Y}_2\text{O}_3, \text{BaCuO}_2, \text{CuO}$	1073	1 d	air	124 major phase + BaCuO_2 + Y_2BaCuO_5	79	[40]
	$\text{Y}_2\text{O}_3, \text{BaCuO}_2, \text{CuO} + 0.2\text{M NaNO}_3 + 10 \text{ drops of dilute HNO}_3$	1088	2 d	O_2	124 single phase		
	$\text{YBa}_2\text{Cu}_3\text{O}_7, \text{CuO}$	1088	10 d	O_2		75	[39]
$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ^c	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1203	3 d	O_2	124 major phase + BaCuO_2		
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1133	8 h	O_2	19 bar	90	[50]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO} + 0.2\text{M NaNO}_3$	1133	5 d	O_2	Single phase	90	[36]
		1133	4 d	O_2	Single phase	90	[36]

^a Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_3\text{O}_7$ are also prepared by this method. Oxygen annealing is carried out below the orthorhombic-tetragonal transition temperature [26, 27].

^b Other rare-earth derivatives of the type $\text{LnBa}_2\text{Cu}_4\text{O}_8$ are obtained by a similar procedure [36, 40].

^c Other rare-earth derivatives of the type $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ are prepared by a similar procedure [36, 38].

such substituted derivatives, the T_c decreases quite rapidly with increasing level of substitution [32, 33].

2.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$ (124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (247) and related cuprates

The first bulk synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ was reported by Karpinski *et al* [34] who heated the mixture of oxides at 1313 K, under an oxygen pressure of 400 bar. Synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ by the conventional ceramic method without the use of high oxygen pressure suffered from some limitations due to kinetic factors. Cava *et al* [35] found that additives such as alkali carbonates enhance the reaction rate. The procedure involves two steps. In the first step Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ and CuO are mixed in the stoichiometric ratio and heated at 1023 K for 16–24 h in an oxygen atmosphere. In the second step, the pre-reacted powder is ground with an approximately equal volume of either Na_2CO_3 or K_2CO_3 powder and pellets of the resulting mixture are heated at 1073 K in flowing oxygen for 3 days. After the reaction, the product is washed with water to remove the excess alkali carbonate and dried by gentle heating in air. The product after this step has $\text{YBa}_2\text{Cu}_4\text{O}_8$ as the majority phase (T_c , 77 K) with little BaCuO_2 impurity. Other reaction rate enhancers such as NaNO_3 , KNO_3 , dilute HNO_3 and Na_2O_2 have also been used successfully (in small quantities) to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ [36–38]. The 124 cuprate can also be prepared without the addition of a rate enhancer by the solid state reaction of Y_2O_3 , BaCuO_2 and CuO at 1088 K in flowing oxygen [36]. Synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ from the solid state reaction between $\text{YBa}_2\text{Cu}_3\text{O}_7$ and CuO in flowing oxygen has also been reported [39]. The synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ by the ceramic method generally takes a long time and requires repeated grinding and pelletizing.

Other rare-earth 124 cuprates, $\text{LnBa}_2\text{Cu}_4\text{O}_8$ with $\text{Ln} = \text{Eu, Gd, Dy, Ho}$ and Er have been prepared by the ceramic method under an oxygen pressure of 1 atm [36, 40]. The T_c of these cuprates decreases with the increasing ionic radius of the rare earth. Calcium can be substituted at the Y site up to 10% in $\text{YBa}_2\text{Cu}_4\text{O}_8$, and the T_c increases from 79 K to 87 K in such substituted $\text{YBa}_2\text{Cu}_4\text{O}_8$ [41]. Lanthanum can be substituted for barium in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [42]. Single phases of $\text{YBa}_{2-x}\text{La}_x\text{Cu}_4\text{O}_8$ have been obtained for $0 \leq x \leq 0.4$ with the T_c decreasing with increase in x .

Extensive studies have been carried out on the synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ under high oxygen pressures [43, 44]. The P – T phase diagram of 124, 123 and 247 cuprates is shown in figure 2. High-oxygen pressure synthesis essentially involves the solid state reaction followed by sintering under high oxygen pressures. The typical sintering temperature and the pressure at which synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ has been carried out are 1200 K and 120 atm of oxygen (for 8 h). By the use of high oxygen pressures [45], it is possible to prepare 124 compounds with other rare earths such as Nd and Sm , which is otherwise not possible under ambient pressures.

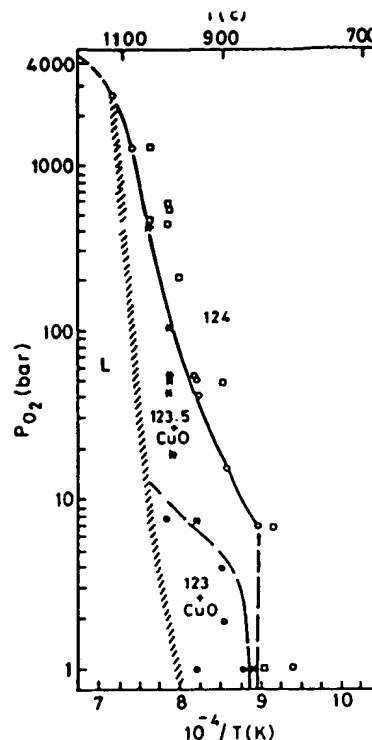


Figure 2. Phase diagram of the 124, 247 and 123 cuprates (from [43]).

A variety of substitutions has been carried out at the Y, Ba and Cu sites in $\text{YBa}_2\text{Cu}_4\text{O}_8$ under high oxygen pressures. Yttrium can be substituted up to 10% by Ca in $\text{YBa}_2\text{Cu}_4\text{O}_8$ giving a T_c of ~ 90 K [46]; 20% Ba has been substituted by Sr without affecting the T_c [47]. Single-phase iron-substituted $\text{YBa}_2\text{Cu}_{4-x}\text{Fe}_x\text{O}_8$ ($0 \leq x \leq 0.05$) has been prepared at an oxygen pressure of 200 bar [48]; the T_c falls monotonically with increasing iron concentration.

Bordet *et al* [49] first reported the preparation of $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ under oxygen pressures of 100–200 bar. It was soon realized that $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ can be synthesized by the ceramic method under an oxygen pressure of 1 atm by a procedure similar to that employed for $\text{YBa}_2\text{Cu}_4\text{O}_8$, except for the difference in the sintering temperature [36]. There is a narrow stability region between 1123 K and 1143 K for the 247 cuprate to be synthesized under 1 atm oxygen pressure. The best sintering temperature at which the 247 cuprate is formed is 1133 K. Other rare-earth 247 cuprates, $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Dy, Er}$), can also be prepared by this method [36, 38]. About 5% of Y can be replaced by Ca in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ and the T_c increases to 94 K [42]. Substitution of La at the Ba site is limited to $\sim 10\%$ in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, where the T_c decreases continuously with increasing lanthanum content [42].

Synthesis of 247 cuprates by the high-pressure oxygen method is generally carried out at 1203 K at an oxygen pressure of around 19 bar (for 8 h). This step is followed by slow cooling (typically 5°C min^{-1}) to room temperature at the same pressure [50]. Other rare-earth 247 compounds, $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ ($\text{Ln} = \text{Eu, Gd, Dy, Ho}$

and Er), have been prepared in the oxygen pressure range of 14–35 bar [50]. Preparative conditions for the 124 and 247 cuprates are given in table 2.

2.4. Bismuth cuprates

Although the ceramic method is widely employed for the synthesis of superconducting bismuth cuprates of the type $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$, it is generally difficult to obtain monophasic compositions, due to various factors [51, 52]. Both thermodynamic and kinetic factors are clearly involved in determining the ease of formation as well as phasic purity of these cuprates. The $n = 1$ member (2201) of the formula $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ appears to be stable around 1083 K and the $n = 2$ member, $\text{Bi}_2(\text{Ca}, \text{Sr})_3\text{Cu}_2\text{O}_8$ (2122) around 1113 K. The $n = 3$ member, $\text{Bi}_2(\text{Ca}, \text{Sr})_4\text{Cu}_3\text{O}_{10}$ (2223), can be obtained close to the melting point (1123 K) after heating for several days or even weeks. Of all the members of the $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$ family, the $n = 2$ member (2122) seems to be most stable. Bi_2O_3 , which is often used as one of the starting materials, melts at around 1103 K. Increasing the reaction temperature therefore leads to preferential loss of volatile Bi_2O_3 . This results in micro-inhomogeneities and the presence of the unreacted oxides in the final product. Since these materials contain so many cations, partial reaction between various pairs of oxides leading to the formation of impurity phases in the final product cannot easily be avoided. A noteworthy structural feature of all these bismuth cuprates is the presence of superlattice modulation; the modulation has nothing to do with superconductivity.

Most of the above problems have been overcome by employing the matrix reaction method [53, 54]. This method reduces the number of reacting components and gives better products. In this method, synthesis is carried out by reacting the oxide matrix made from CaCO_3 , SrCO_3 and CuO with Bi_2O_3 in the temperature range of 1083–1123 K in air for a minimum period of 48 h. Quenching the samples in air from the sintering temperature or heating in a nitrogen atmosphere improves the superconducting properties of bismuth cuprates. The matrix reaction method yields monophasic $n = 2$ (2122) and $n = 3$ (2223) compositions showing T_c values of 85 K and 110 K respectively [55, 56]. Partial melting for a short period (~5 min) also favours the rapid formation of the $n = 2$ (2122) and the $n = 3$ (2223) members.

The $n = 1$ member, $\text{Bi}_2\text{Sr}_2\text{CuO}_6$, showing T_c in the range 7–22 K is a rather complicated system and has two structurally different phases near the stoichiometric composition [51, 57–60]. Many workers have varied the Bi/Sr ratio and obtained single-phase materials with a T_c of 10 K at a composition which is strontium deficient, $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_6$, [60, 61]. This cuprate is best prepared by reacting the oxides and/or carbonates of the constituent metals at 1123 K in air for extended periods of time. In figure 3 we show the phase diagram of the Bi–Sr–Cu–O system. The phase diagram of the

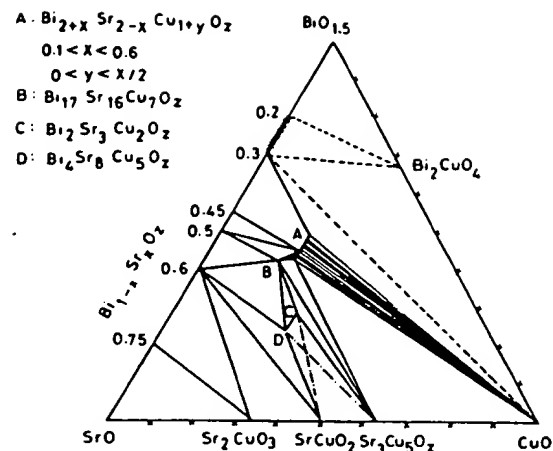


Figure 3. Phase diagram of the Bi–Sr–Cu–O system at 1110 K in air (from [60]).

Bi_2O_3 – SrO – CaO – CuO system at a constant Cu content is shown in figure 4.

Substitution of a small amount of lead for bismuth results in good superconducting samples of $n = 2$ (2122) and $n = 3$ (2223) members. A number of workers have therefore preferred to synthesize both $n = 2$ (2122) and $n = 3$ (2223) members with substitution of lead up to 25% in place of bismuth [58, 63–66]. They are obtained either by direct reaction of oxides and/or carbonates of the cations or by the matrix reaction method.

Other than the matrix reaction method, melt quenching (glass route) [67, 68] and a semi-wet method [6] have been employed for the synthesis of superconducting bismuth cuprates. In the melt quenching method the mixture of starting materials (in the form of oxide and/or carbonates) is melted in a platinum or alumina crucible around 1473 K for a short period in air and then quenched in liquid nitrogen. The quenched specimens are given an annealing treatment around 1103 K in air to obtain the superconducting crystalline cuprates. This method has been shown to produce both $n = 2$ (2122) and lead-doped $n = 3$ (2223) members.

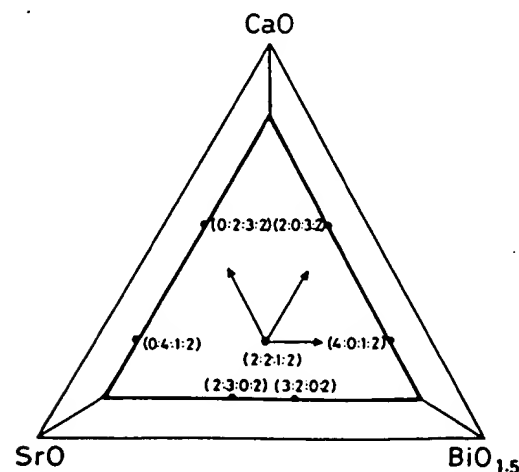


Figure 4. Section through the phase diagram of the Bi_2O_3 – SrO – CaO – CuO system at a constant CuO content of 28.6 mol% (from [62]).

of the bismuth cuprates, essentially in pure form. The semi-wet method involves the solid state reaction between two precursors which are coprecipitated separately. For example, in the preparation of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, a precipitate of Pb, Sr and Ca (as carbonates) and one of Bi and Cu (as oxalates) are reacted at 1138 K in air for a minimum period of 72 h. The duration of the reaction for the formation of 2223 phase is drastically reduced by this method.

The starting composition of the reactant materials plays an important role in the synthesis of these cuprates. For example, strontium deficiency in the $n = 1$ (2201) member favours monophasic compositions [59, 61]. Strontium deficiency also helps in obtaining a phase-pure $n = 2$ (2122) member [70]. Starting with a 4:3:3:4 stoichiometry of Bi:Ca:Sr:Cu, it has been possible to obtain a monophasic 2122 member [54, 71]. The $n = 3$ (2223) phase, on the other hand, is either obtained through the substitution of Bi by Pb (up to 25%) or by taking an excess of Ca and/or Cu [63–66, 72]. The problem of balancing between phasic purity and high T_c of the cuprate gives rise to some difficulty in the synthesis of these cuprates. The coexistence of some of the members of the homologous series, especially in the form of polytypic intergrowths of different layered sequences, is also a problem. This problem is also encountered with thallium cuprates [73, 74].

The $n = 4$ phase, $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_3\text{Sr}_2\text{Cu}_4\text{O}_{12}$, which was observed in an electron micrograph along with $n = 3$ phase as an intergrowth, was synthesized in bulk by Rao *et al* [75] (with a small proportion of the $n = 3$ phase) by the ceramic method. The $n = 4$ phase has a slightly lower T_c (103 K), than the $n = 3$ phase. This cuprate has also been prepared by Losch *et al* [75].

A variety of substitutions has been carried out in superconducting bismuth cuprates employing the ceramic method [58, 76–79]; some of them are noteworthy. For example, the simultaneous substitution of Bi by Pb and Sr by La in $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ results in a modulation-free superconductor of the formula $\text{BiPbSr}_{1+x}\text{La}_{1-x}\text{CuO}_6$ with T_c increased to 24 K [77]. Similarly, co-substitution of Bi by Pb and Ca by Y in the $n = 2$ member (2122) gives a modulation-free superconductor, $\text{BiPbY}_{0.5}\text{Ca}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_8$ with a T_c of 85 K [77]. Rare-earth substitution for Ca in $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ causes the T_c to go up to 100 K without the introduction of the $n = 3$ phase [58, 78]. As mentioned earlier, the $n = 3$ phase is stabilized by the partial substitution of lead in place of bismuth [63–65]. Another significant discovery is the iodine intercalation of the Bi-2122 superconductor [80]. Intercalation does not greatly affect the superconducting properties of the material; clearly, superconductivity is confined to the two-dimensional CuO_2 sheets in these materials.

Synthesis of a new series of superconducting cuprates of the general formula $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$ (Bi-2222 phase with Ln = Sm, Eu, Gd) containing a fluorite-like $(\text{Ln}_{1-x}\text{Ce}_x)_2\text{O}_2$ layer between the two CuO_2 sheets has been possible by the ceramic method [81]. Partial substitution of bismuth by lead increases

the T_c of this phase to 50 K [62]. High-pressure synthesis at 80 atm of O_2 seems to stabilize the 2222 structure with other rare earths [83].

As mentioned earlier, one does not start with an exact stoichiometric composition to obtain the desired final product in the case of superconducting bismuth cuprates. Although structural studies (see for example [84]) indicate the presence of bismuth atoms over strontium and calcium sites as well, it is not possible to prescribe an exact initial composition to obtain the desired final stoichiometry. For example, starting from a nominal composition of $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_2\text{O}_y$, one ends up with the formation of the $n = 3$ (2223) member [65]. Therefore, for the purpose of characterizing the various members of the superconducting bismuth cuprates, one starts with some arbitrary composition and varies the synthetic conditions suitably to obtain the desired final product in pure form. The actual compositions of the final cuprate are quite unexpected (e.g. $\text{Bi}_{1.83}\text{Pb}_{0.30}\text{Sr}_{2.04}\text{Ca}_{1.68}\text{Cu}_3\text{O}_y$) as found from analytical electron microscopy [85]. In table 3 we have summarized the preparative conditions of all the members of $\text{Bi}_2(\text{Ca, Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$ family.

2.5. Thallium cuprates

The conventional ceramic method employed for the synthesis of 214, 123 and bismuth cuprates has to be modified in the case of thallium cuprates of the $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$, $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ and $\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$ families due to the toxicity and volatility of thallium oxide. In the early days, the reaction was carried out in an open furnace in air or oxygen atmosphere at high temperatures (1150–1180 K) for 5–10 min [86, 87]. In a typical procedure, the mixture of reactants in the form of a pellet was quickly introduced into the furnace maintained at the desired temperature. Since melt–solid reactions take place faster than solid–solid reactions, the product was formed quickly by this method [87]. Although this method requires a very short duration of heating, it results in the loss of thallium, leading to the danger of inhaling thallium oxide vapour. Some workers have taken certain precautions not to release the Tl_2O_3 vapour into the open laboratory, but the method is still not recommended. Furthermore, the formation of the desired phase is not ensured under the open reaction conditions. Synthesis of thallium cuprates has therefore been carried out in closed containers (sealed tubes) by most workers. By this method, both polycrystalline samples and single crystals can be prepared, since the reaction is carried out over longer periods. Better control of stoichiometry, homogeneity of phases and the total avoidance of the inhalation of toxic thallium oxide vapours are some of the advantages of carrying out sealed tube reactions.

Closed reaction conditions have been achieved in different ways. The reactant mixture is sealed in gold [88] or silver tubes [89] or in a platinum [90] or nickel

Table 3. Preparative conditions for the synthesis of bismuth cuprates by the ceramic method.

Starting composition	Conditions ^a		Product	T_c (K)	Ref.
	Temp. (K)	Time			
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1103	2 d	2201 major phase	20	[51]
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	1123	1 d	2201 major phase	9	[57]
$\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_x$	1123	2 d	Single phase	10	[59, 61]
$\text{BiPbSr}_{1-x}\text{La}_{1-x}\text{CuO}_6$	1150	1 d	Single phase	24	[77]
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	1103	5 d	Single phase	85	[61]
$\text{Bi}_2\text{Ca}_{1.5}\text{Sr}_{1.5}\text{Cu}_2\text{O}_8^b$	1103	3 d	2122 major phase	80	[53]
$\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_x$	1108	2 d	2122 single phase	85	[71]
$\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_x$	1113	3 d	2122 single phase	85	[70]
$\text{BiPbSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$	1200	1 d	2122 single phase	85	[77]
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_x^b$	1140	5 d	2223 major phase	120	[55]
$\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Ca}_{2.5}\text{Sr}_{1.5}\text{Cu}_3\text{O}_x^b$	1100	4 d	2223 major phase	105	[64]
$\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_x$	1153	10 d	2223 single phase	110	[72]
$\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_{1.8}\text{O}_x$	1153	5 d	2223 major phase	105	[65]
$\text{BiCaSrCu}_2\text{O}_x$	1143	5 d	2223 major phase	120	[65]
$\text{Bi}_{3.2}\text{Pb}_{0.8}\text{Ca}_5\text{Sr}_4\text{Cu}_7\text{O}_x$	1133	5 d	2223 major phase	108	[64]
$\text{Bi}_2\text{Gd}_{1.7}\text{Ce}_{0.3}\text{Sr}_3\text{Cu}_2\text{O}_{10}$	1273	10 h	2222 single phase	30	[81]

^a All the preparations carried out in air.^b Obtained by matrix reaction method.

alloy (Inconel) container [91] closed tightly with a silver lid. Alternatively, the reactant mixture is taken in the form of a pellet, wrapped in a platinum [92] or gold [93] foil and then sealed in a quartz tube. This method has the advantage of carrying out the reaction under a vacuum. Some workers place the reactant pellet in an alumina crucible [94] which is then sealed in a quartz ampoule. Thallium-excess starting compositions have been employed by a few workers to compensate for the thallium loss during the reaction [95].

In the preparation of the thallium cuprates, the matrix reaction method is often employed. Here, a mixed oxide containing all the metal ions other than the volatile thallium oxide is first prepared by reacting the corresponding oxides and/or carbonates around 1200 K for 24 h in air [89, 96]. The freshly prepared mixed oxide is then taken with a calculated quantity of Tl_2O_3 and heated at appropriate temperatures in a sealed tube. This method is desirable when a carbonate is used as the starting material. Some of the thallium cuprates have been prepared by a modified matrix method [97] wherein a thallium-containing precursor such as $\text{Ba}_2\text{Tl}_2\text{O}_5$ is prepared first and then reacted with other components under closed conditions. Thallium-containing precursors are less volatile than Tl_2O_3 so that the loss of thallium is minimized during the preparation.

Thermodynamic and kinetic factors associated with the synthesis of thallium cuprates are complex due to the existence of various phases which are structurally related and which can therefore intergrow with one another. In fact, one of the common defects that occurs in the thallium cuprates is the presence of random intergrowths between the various layered phases [98]. Furthermore, many of the thallium, lead and bismuth superconductors are metastable phases which are entropy stabilized [99]. The temperature of the reac-

tion, the sintering time and the starting composition are therefore all crucial to obtaining monophasic products (table 4).

The effect of the starting composition is best illustrated by the formation of the $n = 3$ phase of the bilayer thallium cuprates ($\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$). Synthesis of this compound starting from the stoichiometric mixture of the oxides corresponding to the ideal composition often yields the $n = 2$ member of the family. It was found that starting with compositions rich in Ca and/or Cu (namely $\text{TlCa}_3\text{BaCu}_3\text{O}_7$, $\text{Tl}_2\text{Ca}_4\text{Ba}_2\text{Cu}_5\text{O}_9$) yielded a nearly pure $n = 3$ phase [90, 98, 100]. The actual composition is, however, close to $\text{Tl}_{1.7}\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_9$. In the case of $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$ (1122) starting from a stoichiometric mixture of oxides corresponding to the ideal stoichiometry always yielded a mixture of 1122 and 2122 phases, the relative proportion of the two being dependent on the conditions. It has been demonstrated recently [101] that thallium-deficient compositions corresponding to $\text{Tl}_{1-x}\text{CaBa}_2\text{Cu}_2\text{O}_7$ ($\delta = 0.0$ to 0.3) yield better monophasic 1122 materials.

The thallium content of the material not only determines the number of Tl-O layers but controls the hole concentration. As mentioned earlier, one of the good starting compositions to obtain $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (2223) is $\text{TlCa}_3\text{BaCu}_3\text{O}_7$ (1313) which bears little relation to the composition of the final product. Another example is the formation of the $n = 4$ phase, $\text{TlCa}_3\text{Ba}_2\text{Cu}_4\text{O}_9$ (1324). Detailed studies [102] have shown that the 2223 phase formed initially transforms to the 1223 phase with an increase in the duration of heating. After prolonged sintering, the 1324 phase is formed at the expense of the 1223 phase. Similar transformations have also been observed in the formation process of $\text{TlCa}_4\text{Ba}_2\text{Cu}_5\text{O}_9$ with five Cu-O layers [103].

The Sr analogue of $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ cannot be prepared in pure form. However, they are stabilized by

Starting composition	Conditions			Product	T_c (K)	Ref.
	Temp. (K)	Time	Gas			
$Tl_2Ba_2CuO_6$	1148	3 h	Sealed gold tubes	2201 single phase	84	[88]
$Tl_2CaBa_2Cu_2O_8$	1173	6 h	Sealed gold tubes	2122 single phase	98	[88]
	1150	3 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_4Ba_2Cu_5O_{10}$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_4Ca_3Ba_4Cu_5O_{10}$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_2Cu_3O_{10}$	1173	6 h	Sealed gold tubes	2223 major phase	105	[88]
	1123	20 min	Sealed silica ampoule	2223 major phase	106	[95]
	1103	12 h				
$TlCa_3BaCu_3O_7$	1153	3 h	Sealed silica ampoules	2223 major phase	125	[100]
$Tl_2CaBa_2Cu_3O_7$	1153	3 h	Sealed silica ampoules	2223 major phase	108	[100]
$TlBa_{1-x}La_{0.5x}CuO_5$	1163	3 h	Sealed silica ampoules	1021 single phase	40	[111]
$TlSrLaCuO_5$	1170	2 h	Sealed silica ampoules	1021 single phase	40	[109]
$TlSr_{2-x}Nd_{0.4x}Cu_2O_4$	1170	2 h	Sealed silica ampoules	1122 major phase	80	[110]
$TlCaBa_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 major phase + 2122 impurity	90	[101]
$Tl_{0.8}CaBa_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 major phase	90	[101]
$(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 single phase	90	[104]
$Tl(Ca_{0.5}Y_{0.5})Sr_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 single phase	90	[92]
$TlCa_2Ba_2Cu_3O_9$	1163	6 h	Sealed silica ampoules	1223 single phase	115	[94]
$(Tl_{0.5}Pb_{0.5})Ca_2Sr_2Cu_3O_9$	1198	3–12 h	Sealed gold tubes	1223 single phase	122	[105]
$Tl_{0.5}Pb_{0.5}Sr_4Cu_3O_8$	1170	2 h	Sealed silica ampoules	1223 major phase	60	[110]

partly substituting Tl by Pb (or Bi) or Ca by yttrium or a trivalent rare earth [92, 104–107]. Thus, $Tl_{0.5}Pb_{0.5}Ca_{n-1}Sr_2Cu_nO_{2n+3}$ shows a T_c of ~ 90 K for $n = 2$ and ~ 120 K for $n = 3$. $TlCa_{0.5}Y_{0.5}Sr_2Cu_2O_7$ also shows a T_c of 90 K. These cuprates in the Tl/Pb–Ca/Ln–Sr–Cu–O systems are prepared in a manner similar to the Tl–Ca–Ba–Cu–O system except that $SrCO_3$ is used in place of $BaCO_3$ or BaO_2 . $Sr_4Tl_2O_7$ has also been used as a starting material in some instances [97]. The $n = 1$ member, TlM_2CuO_5 ($M = Sr$ or Ba) is also stabilized by the substitution of Pb or Bi for Tl or a trivalent rare earth for Sr or Ba [108–111]. All these compounds showing a T_c of 40 K have been prepared by the matrix reaction method.

Single thallium layer cuprates of the general formula $Tl_{1+x}A_{2-x}Ln_2Cu_2O_9$ with $A = Sr, Ba$; $Ln = Pr$ (Nd, Ce) as well as $Tl_{0.5}Pb_{0.5}(Ln_{1-x}Ce_x)_2Sr_2Cu_2O_9$ ($Ln = Pr, Gd$) with a fluorite-type Ln_2O_3 layer have been prepared by the ceramic method [112, 113]. The as-prepared materials are semiconductors. It has been shown by Liu *et al* [114] that annealing $TlBa_2(Eu, Ce)_2Cu_2O_9$ (1222 phase) under an oxygen pressure of 100 bar induces superconductivity with a T_c of ~ 40 K.

As in the case of bismuth cuprates, the final composition of thallium cuprates is unlikely to reflect the composition of the starting mixture. Structural studies [99, 115] have shown that there is cation disorder between Tl and Ca/Sr sites. Therefore, in order to obtain a superconducting composition corresponding to a particular copper content, one has to start with various arbitrary compositions and vary the synthesis conditions. The actual composition of the final product can be quite unexpected (e.g. $Tl_{1.83}Ba_2Ca_{1.44}Cu_3O_9$ or $Tl_{1.86}Ba_{2.01}CuO_9$) as shown by analytical electron microscopy [85]. In table 4 we have listed the pre-

parative conditions employed for the synthesis of thallium cuprates by the ceramic method.

2.6. Lead cuprates

The conditions for the synthesis of superconducting lead cuprates are more stringent than for the other copper oxide superconductors. Direct synthesis of members of the $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$ ($Ln = Y$ or rare earth) family by the reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 1173 K is not possible because of the high stability of $SrPbO_3$ -related perovskite oxides. Preferential loss of the more volatile PbO leads to micro-inhomogeneities. Furthermore, Pb in these compounds is in the 2+ state while part of the Cu is in the 1+ state. Synthesis has therefore to be carried out under mildly reducing conditions, typically in an atmosphere of N_2 containing 1% O_2 . The most common method that has been employed for the synthesis of these lead cuprates is the matrix reaction method [116]. For $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$ ($Ln = Y$ or rare earth), a mixed oxide containing all the metal ions except Pb is made by reacting $SrCO_3$, Ln_2O_3 or Y_2O_3 , $CaCO_3$ and CuO in the appropriate ratios around 1223 K in air for 16 h. The mixed oxide is then taken with an appropriate amount of PbO, ground thoroughly, pelletized and heated in the 1133–1198 K range in a flowing stream of nitrogen containing 1% O_2 for periods between 1 and 16 h. Generally, short reaction times and quenching the product from the sintering temperatures into liquid nitrogen in the same atmosphere gives better-quality samples. Even though this is the common method for preparing $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+\delta}$, it is not always easy to obtain samples exhibiting good, reproducible

superconducting properties. The lead cuprates from the method described above generally show broad transitions in the R - T curves with negative temperature coefficients of resistance above T_c .

Studies of the dependence of T_c on the calcium concentration in the $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$ system [117] have shown that heating the samples near the melting point between 1198 and 1228 K for 2 h and post-annealing in flowing nitrogen gas at a temperature between 673 and 773 K improves the superconducting properties of the samples dramatically. Direct one-step synthesis has been achieved [118] by reacting the metal oxides in sealed gold tubes around 1223 K. An alternative route to the direct synthesis from metal oxides and/or carbonates has also been demonstrated [119]. Superconductivity near 70 K has been reported in Ca-free $\text{Pb}_2\text{Sr}_2\text{LnCu}_3\text{O}_{8+\delta}$ ($\text{Ln} = \text{Y}$ or rare earth) employing the vacuum annealing procedure [120]. Substitution of Pb by Bi in $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$ has also been carried out by the ceramic method [121]. About 30% of Pb can be substituted by Bi, and such a substitution increases the T_c up to 100 K. The $n = 0$ member of the $\text{Pb}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Ln}_x)\text{Cu}_{2+n}\text{O}_{6+2n+\delta}$ series (namely $\text{Pb}_2(\text{SrLa})\text{Cu}_2\text{O}_{6+\delta}$) has been prepared successfully by this matrix reaction method [122].

Unlike the 2213-type lead cuprates, superconducting 1212-type lead cuprates of the formula $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$ are synthesized in an oxidizing atmosphere. Several authors have reported direct synthesis as well as reactions under closed conditions [123–127]. In the direct synthesis of these cuprates, care is taken to prevent the loss of Pb by wrapping pellets in gold or platinum foil [127]. Rouillon *et al* [125, 126] have reported the synthesis of 1212 lead cuprates by the direct reaction of the component oxides in evacuated silica ampoules. This method has

the advantage of adjusting the oxygen partial pressure required for the synthesis. Both 2213-type and 1212-type lead cuprates have been prepared using the nitrates of the metal ions as the starting materials [128]. Although this procedure yields 2213 or 1212 phases in a single step, the product obtained always has impurities such as Y_2O_3 , CuO etc.

A superconducting lead cuprate of the formula $(\text{Pb}, \text{Cu})(\text{Eu}, \text{Ce})_2(\text{Sr}, \text{Eu})_2\text{Cu}_2\text{O}_9$ (1222 phase) containing a fluorite layer has been prepared by the direct reaction of the component metal oxides at 1273 K in oxygen atmosphere [129].

High-pressure ceramic synthesis has been employed to prepare lead cuprates of the 1212 type [130, 131]. In order to prepare $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$, sintering is carried out at 1213 K for 15 h under an oxygen pressure of 100 bar followed by fast cooling to 373 K. The samples obtained from high-pressure oxygen treatment show higher T_c s than those processed at 1 bar pressure of oxygen. Substitution of Y by other rare earths has been possible by this high-oxygen-pressure method [131]. All the rare-earth substituted compounds are superconducting with T_c s in the 50–70 K range. The T_c decreases with increase in the size of the rare earth. In table 5 we summarize the conditions for the synthesis of the various lead cuprates by the ceramic method.

2.7 Electron-doped superconductors

All the cuprates discussed till now are hole superconductors. Synthesis of electron-doped cuprate superconductors of the type $\text{Ln}_{2-x}\text{M}_x\text{CuO}_{4-\delta}$ ($\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$; $\text{M} = \text{Ce}, \text{Th}$), possessing the T' structure, is generally achieved by the ceramic method [132–134]. The conditions of synthesis are more stringent since the

Table 5. Conditions for the synthesis of lead cuprates by the ceramic method.

Compound	Starting materials	Conditions			Comments	T_c (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$ matrix	1143	1–16 h	$\text{N}_2 + 1\% \text{O}_2$		78	[116]
	$\text{PbO}, \text{PbO}_2, \text{CaO}_2, \text{SrO}_2, \text{Y}_2\text{O}_3, \text{CuO}$	1223	12–48 h		Sealed gold tubes	78	[118]
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1073	15 h	air			
		1173	2 h	air			
		1073	1–5 h	N_2		78	[119]
$\text{Pb}_2\text{Sr}_{0.8}\text{La}_{1.2}\text{Cu}_2\text{O}_{8+\delta}$	$\text{PbO}, \text{La}_2\text{O}_3, \text{Sr}_2\text{CuO}_3, \text{CuO}$	1083	6 h	N_2	2202 major phase + $\text{Pb}_2\text{LaCu}_{0.3}\text{O}_7$ impurity	26	[122]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{SrLaCuO}_4$	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3, \text{CuO}$	1073	5 h	air			
		1273	2 h	O_2		25	[123]
$(\text{Pb}_{0.7}\text{Cu}_{0.3})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-\delta}$	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CuO}$	1123	10 h	air			
		1273	1 h	O_2	1212 major phase + $\text{Sr}_5\text{Pb}_3\text{CuO}_{12}$ impurity	50	[124]
	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_{2.3}\text{O}_7$ matrix	1243	3 h	O_2	1212 major phase + $\text{Sr}_5\text{Pb}_3\text{CuO}_{12}$ impurity	47	[127]
$(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{PbO}, \text{PbO}_2, \text{Sr}_2\text{CuO}_3, \text{Y}_2\text{O}_3, \text{CaO}_2, \text{Cu}_2\text{O}, \text{CuO}$	1108–1223	1–10 h		Evacuated silica tubes	100	[125]
$(\text{Pb}_{0.5}\text{Ca}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{PbO}_2, \text{PbO}, \text{SrO}_2, \text{SrCuO}_2, \text{Y}_2\text{O}_3, \text{CaO}, \text{CuO}$	1108–1223	1–10 h		Evacuated silica tubes	80	[126]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1.75}\text{Eu}_{0.25})\text{Cu}_2\text{O}_7$	$\text{PbO}, \text{SrCO}_3, \text{Eu}_2\text{O}_3, \text{CeO}_2, \text{CuO}$	1123	10 h	air	Single phase	25	[129]
		1323	1 h	O_2	1222		

valence of copper has to be less than 2+ in the material, by making sure that the extra electron donated by Ce^{4+} or Th^{4+} does not increase the oxygen content of the cuprate. For this reason, samples after calcination and sintering at 1323 K in air (for 24 h) are annealed in a reducing atmosphere (typically Ar, N_2 or dilute H_2) at 1173 K to achieve superconductivity. Samples prepared in this manner show a negative temperature coefficient of resistance above T_c in the R - T curves; the resistivity drop at T_c is also not sharp. An alternative synthetic route involves the reaction of pre-reacted $NdCeO_{3.5}$ material with the required amounts of Nd_2O_3 and CuO at 1253 K for a minimum period of 48 h in flowing oxygen [135]. The samples are then rapidly quenched from 1253 K in an argon atmosphere to achieve superconductivity. This procedure eliminates the slow diffusion of Ce throughout the Nd_2CuO_{4-x} host and gives uniform concentrations of cerium and oxygen. Samples obtained from this route show a sharp transition at 21 K.

Superconductivity with a T_c of 25 K is induced by doping fluorine for oxygen in Nd_2CuO_4 . This has been accomplished by taking NdF_3 as one of the initial reactants [136]. Substitution of either Ga or In for copper in non-superconducting $Nd_{2-x}Ce_xCuO_{4-x}$ also induces superconductivity [137, 138].

2.8. Infinite-layer cuprates

Discovery of superconductivity in cuprates containing infinite CuO_2 layers has been of great importance in understanding the phenomenon. Very high pressures have been employed for obtaining the infinite-layer cuprates. Both hole-doped (e.g. $Ca_{1-x}Sr_xCuO_2$) and electron-doped ($Sr_{1-x}Nd_xCuO_2$) infinite-layer cuprate superconductors with a maximum T_c of 110 K have been reported [139–142]. Infinite-layered cuprates of the type $(Ba, Sr)CuO_2$, $(Ca, Sr)CuO_2$ are synthesized in an oxidizing atmosphere under high hydrostatic pressure [139, 140, 142]. Electron-doped $Sr_{0.86}Nd_{0.14}CuO_2$ is also prepared under high hydrostatic pressures [141]. Metal nitrates are generally used as the starting materials since carbonates of Ba, Sr and Ca have high decomposition temperatures. After decomposing the metal nitrates at around 873–1123 K in air, the product is subjected to high pressure to obtain the superconducting phases. $Sr_{0.86}Nd_{0.14}CuO_2$, which superconducts at 40 K, is made under a hydrostatic pressure of 25 kbar at 1273 K. Superconducting $(Ca, Sr)CuO_2$ is prepared at 1273 K under 6 GPa pressure. Deficiency of Sr and Ca as well as the oxidizing atmosphere make this phase superconducting, and the oxidizing atmosphere is provided by heating a capsule containing $KClO_4$ along with the sample. This cuprate has a T_c (onset) of 110 K.

3. Coprecipitation and precursor methods

Coprecipitation involves the separation of a solid containing various ionic species chemically bound to one

another from a liquid or a solution phase. A homogeneous coprecipitation process can result in the formation of crystalline or amorphous solids. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

(i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.

(ii) The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for coprecipitation of oxidic materials are carbonates, oxalates, citrates etc. The same is true of high- T_c cuprates. The precipitates in some instances could be genuine precursors or solid solutions [5, 6]. It is well known that precursor solid solutions drastically bring down diffusion distances for the cations and facilitate reactions in the solid state. We shall not distinguish precursor solid solutions precipitated from solutions from other precursors in this discussion.

The precipitates (carbonate, oxalate etc) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired cuprate. Some of the advantages of the coprecipitation technique over the ceramic method are an homogeneous distribution of components, a decrease in the reaction temperatures and of the duration of annealing, a higher density and a lower particle size of the final product. The major drawback of this route is the control over the stoichiometry of the final product.

3.1. $La_{2-x}Sr_xCuO_4$

La, Sr and Cu in $La_{2-x}Sr_xCuO_4$ are readily coprecipitated as carbonates [11, 12, 143]. For this purpose the required quantities of the various metal nitrates are dissolved together in distilled water. Alternatively, the corresponding oxides are dissolved in nitric acid to give a nitrate solution and the pH of the solution is adjusted to 7–8 by the addition of KOH solution. A solution of K_2CO_3 of appropriate strength is then slowly added under stirring to give a light blue precipitate which is thoroughly washed. The precipitate is dried at 420 K and calcined at 1070 K for 8 h in air. The resulting black powder is ground and pelletized and sintered at 1270 K for 16 h in air to obtain monophasic $La_{1.85}Sr_{0.15}CuO_4$, superconducting at 35 K.

Instead of as carbonate, the metal ions are also readily precipitated as oxalate by the addition of either oxalic acid or potassium oxalate to the solution of metal nitrates [11, 12, 144, 145]. The precipitated oxalate is then decomposed to obtain the cuprate. This method has certain disadvantages:

(i) La^{3+} in the presence of an alkali metal oxalate first yields lanthanum oxalate which further reacts with the precipitating agent to give a double salt. Control of stoichiometry therefore becomes difficult, leading to multiphasic products.

(ii) The relative solubilities of some of the oxalates also pose difficulties. For example, SrC_2O_4 is nearly four times more soluble than SrCO_3 .

3.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

$\text{YBa}_2\text{Cu}_3\text{O}_7$ and related 123 compounds can be obtained via coprecipitation of the component metals (from a nitrate solution) as a formate [146, 147], acetate [148], oxalate [12, 149–156], hyponitrite [157] or hydroxycarbonate [158, 159]. Some of these precipitates could be genuine precursor compounds as is indeed the case with the hyponitrite.

In oxalate coprecipitation [12, 149–152], oxalic acid solution of appropriate concentration is added to an aqueous solution of mixture of nitrates of Y, Ba and Cu and the pH of the solution is adjusted to 7.5 (by dilute NH_3). The pale green slurry thus formed is digested for 1 h, filtered and dried. The oxalate is converted to orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating at 1053 K in air for 5 days followed by oxygenation at 723 K. This procedure, even though successful in making superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in small particulate form, often results in undesirable stoichiometry because of the moderate solubility of barium oxalate. Furthermore, rare-earth ions in the presence of ammonium oxalate give a double salt with the excess oxalate which competes with the precipitation of copper and barium oxalates. These difficulties can be overcome either by taking a known excess (wt%) of barium and copper or by using triethylammonium oxalate as the precipitant in aqueous ethanol medium [153–155]. The alcoholic medium decreases the solubility of barium oxalate and the pH of the solution is controlled *in situ*.

A better method of homogeneous coprecipitation of oxalates is that of Liu *et al* [156] using urea and oxalic acid. Urea, on heating, is hydrolysed liberating CO_2 and NH_3 , and thus gradually adjusting the pH throughout the solution. The CO_2 liberated controls the bumping of the solution during digestion. The oxalate coprecipitation route is widely described in the literature. The reactive powders obtained by the oxalate coprecipitation method decrease the sintering temperature. The formation of BaCO_3 in the intermediate calcinating step makes it difficult to obtain $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in pure form.

Complete avoidance of the formation of BaCO_3 during the synthesis is possible using the hyponitrite precursor [157]. The hyponitrite precursor is obtained from a nitrate solution of Y, Ba and Cu ions by the addition of an aqueous $\text{Na}_2\text{N}_2\text{O}_2$ solution. The precipitate is converted into superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating at around 973 K in an argon atmosphere, followed by oxygen annealing at 673 K. Although this route provides a convenient means of obtaining the 123 cuprate at much lower temperatures than with other methods, there is a possibility of contamination of alkali metal ions during the course of the precipitation.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ can also be prepared by the hydroxycarbonate method [158, 159]. Here, KOH and K_2CO_3

are employed to precipitate copper as the hydroxide and Y and Ba as the carbonates in the pH range of 7–8. By employing NaOH and Na_2CO_3 , complete precipitation as hydroxycarbonate is attained at a pH of ~13. The product from the above two procedures is homogeneous, showing sharp onset of superconductivity at 92 K. The possibility of contamination by alkali metal ions cannot, however, be avoided.

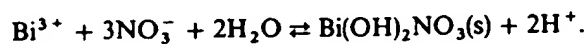
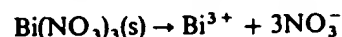
3.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

$\text{YBa}_2\text{Cu}_4\text{O}_8$ can be prepared by the oxalate route [160] wherein the solution of Y, Ba and Cu nitrates in water is added dropwise into oxalic acid–triethylamine solution under stirring. Complete precipitation of Y, Ba and Cu with the desired stoichiometry of 1:2:4 is achieved in the pH range of 9.3–11.3. The precipitated oxalates are filtered and dried in air at 393 K. The solid obtained is then heated in the form of pellets at 1078 K in flowing oxygen for 2–4 days. The product after quenching in air shows the 124 phase as the major product with a T_c of 79 K.

An alternative coprecipitation route for the synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ is the method of Chen *et al* [161] in which the aqueous nitrate solution of the constituent metal ions is mixed with 8-hydroxyquinoline-triethylamine solution. The precipitated oxine is filtered, washed, dried and sintered at 1088 K in oxygen for 3 days to yield phase-pure $\text{YBa}_2\text{Cu}_4\text{O}_8$ showing a T_c of 80 K. Ethylenediaminetetraacetic acid [161] as well as carbonate routes [162] have also been employed for the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$. Coprecipitation using triethylammonium oxalate has been exploited for substituting Sr in place of Ba in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [163].

3.4. Bismuth cuprates

Very few coprecipitation studies have been carried out on the preparation of bismuth cuprates. One reason may be that despite the good sample homogeneity generally obtained through solution methods, the chemistry of bismuth cuprates is rather complex. It is not that easy to find compounds of all the constituent metal ions soluble in a common solvent; controlling the stoichiometry in these cuprates is also difficult in the coprecipitation procedure. Furthermore, bismuth nitrate, which is often used as one of the starting materials, decomposes in cold water to a basic nitrate precipitate as given by



This problem can be overcome to some extent by preparing the nitrate solution of bismuth in nitric acid or by starting with bismuth acetate instead of the nitrate.

Bidentate ligands such as the oxalate are found to react more rapidly than multidentate ligands such as citric acid [164–174] in the coprecipitation process. Complexes of oxalic acid are also more stable than

those obtained from a monocationic agent such as acetic acid, but there are some difficulties in controlling the stoichiometry because of the relative solubility of BiC_2O_4 or SrC_2O_4 .

A straightforward oxalate coprecipitation is achieved by dissolving the acetates of Bi, Ca, Sr and Cu in glacial acetic acid and then adding excess oxalic acid to the solution [164]. The oxalate precipitate is dried and decomposed at around 1073 K in air and processed in the 1103–1123 K range for periods ranging from 24 h to 4 days, depending on the starting composition. The $n = 2$ (2122) member obtained by this procedure shows zero resistance at 83 K. In another procedure reported by Zhang *et al* [165], first the Sr/Ca/Cu nitrate solutions are mixed in the required molar ratio. Into this solution is poured a solution of bismuth nitrate prepared in nitric acid along with oxalic acid. The complete precipitation occurs at a pH of around 5 (attained by the addition of aqueous NaOH). This process involves the possibility of contamination of sodium ions; this has been circumvented by using $\text{N}(\text{CH}_3)_4\text{OH}$ to adjust the pH of the solution [166] and complete precipitation of the oxalates occurs at a pH of 12. All these procedures, however, produce mixed-phase samples.

For the preparation of the monophasic lead-doped $n = 3$ member (2223), oxalate coprecipitation has been found effective [167–174]. In the procedure reported by Chiang *et al* [171], the molar ratio of the chelating agent (oxalic acid) and the nitrate anions (from the metal nitrate solutions) is fixed at 0.5 and the pH, adjusted by NH_4OH solution, at which complete precipitation occurs is 6.7. The product from this method, $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_7$, after sintering at 1133 K in air for 72 h, shows a T_c of 110 K.

Coprecipitation as oxalates to prepare the lead-doped $n = 3$ member (2223) has been achieved from an ethylene glycol medium using triethylammonium oxalate and oxalic acid [172]. A more easily controlled and reproducible oxalate coprecipitation procedure appears to be that of Shei *et al* [173] where in a mixture of triethylamine and oxalic acid is employed. The advantage of using triethylamine is that it has a higher basicity and a lower complexing ability towards Cu(II) than has ammonia. Control of the stoichiometry of the final product is therefore better obtained with this procedure; precipitation occurs in the pH range 1.5–2.2. The coprecipitated oxalates sintered at 1133 K in air for a minimum period of 72 h give monophasic $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with a T_c of 110 K. It is possible to avoid adjusting the pH in the coprecipitation of oxalates [174]. The procedure involves coprecipitating the oxalates from dilute acetate solutions instead of from nitrate solutions. The oxalates are then converted to nearly phase-pure $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (T_c of 106 K) by sintering at 1123 K in air for 160 h.

Carbonate coprecipitation has also been carried out for the synthesis of superconducting bismuth cuprates [175, 176], but the method does not yield monophasic products.

Coprecipitation of thallium-based cuprates from aqueous solutions as oxalates is hindered by the solubility of thallium oxalate. However, Bernhard and Gritzner [177] have found that complete coprecipitation as oxalates can be achieved by starting with thallium acetate in glacial acetic acid medium. In the procedure reported for the preparation of the $n = 3$ member (2223), stoichiometric amounts of thallium acetate, CaCO_3 , BaCO_3 and copper acetate are dissolved in water containing glacial acetic acid. The solution containing all the cations is then added to a solution of oxalic acid (excess) under stirring. The precipitate, after digestion for 1 h, is filtered, washed and dried. The oxalates are heated in the form of pellets (wrapped in gold foil) at around 1173 K for 6 min in an oxygen atmosphere. The product after annealing in the same atmosphere shows 2223 as the major phase with a T_c of 118 K.

3.6. Lead cuprates

Carbonate coprecipitation is found to be satisfactory for the synthesis of representative members of superconducting lead cuprates [128] of 2213 and 1212 types, namely $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$ and $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-\delta}$. Coprecipitation as carbonates has been achieved by adding the nitrate solution of the constituent metal ions to an aqueous solution of sodium carbonate (in excess) under constant stirring. The carbonate precipitate thus obtained is washed and dried. The decomposed powder is heated in the form of pellets around 1153 K in a suitable atmosphere. $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$ obtained by this method after heating for 4 h in nitrogen containing 1% O_2 showed 2213 as the major phase ($T_c \sim 74$ K) with impurities such as Y_2O_3 , CuO. The 1212 phase obtained after heating in oxygen at 1153 K for 12 h showed a broad transition with a T_c (onset) of 100 K. This method has the advantage of single heating rather than the multistep procedures required in the other methods.

4. Sol-gel process

The sol-gel process is employed in order to get homogeneous mixing of cations on an atomic scale so that the solid state reaction occurs to completion in a short time and at the lowest possible temperature. The term sol often refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component which has the internal network structure wherein both the solid and the fluid components are highly dispersed. In the sol-gel process a concentrated sol of the reactant oxides or hydroxides is converted to a semi-rigid gel by removing the solvent. The dry gel is heated at an appropriate

temperature to obtain the product. Most of the reactions in the sol-gel process occur via hydrolysis and polycondensation.

Two different routes for the sol-gel process are usually described in the literature for the synthesis of high- T_c cuprate superconductors:

- (i) Via molecular precursors (e.g. metal alkoxides) in organic medium;
- (ii) Via ionic precursors in aqueous medium (citrate gel process).

The purity, microstructure and physical properties of the product are controlled by varying the precursor, solvent, pH, firing temperatures and atmosphere of heat treatment.

4.1. 214 Cuprates

Superconducting 214 compounds are prepared both by means of organometallic precursor [178] and by the citrate gel process [11]. Lanthanum 2,4-pentanedionate, barium 2,4-pentanedionate and copper (II) ethyl hexanoate are mixed at room temperature in the appropriate ratios in methoxyethanol medium to obtain the organometallic precursor. After vigorous stirring at room temperature, the precursor gel is converted to monophasic $\text{La}_{1.9}\text{Ba}_{0.1}\text{CuO}_4$ (T_c 23 K) by firing at 873 K in oxygen.

In the citrate gel process, a mixture of citric acid and ethylene glycol is added to the solution containing the required quantities of metal nitrates. The resulting solution is vigorously stirred and heated around 393 K. During this process, oxides of nitrogen evolve, resulting in a viscous gel. The gel is decomposed at 673 K in air and the resulting black powder is then given the necessary heat treatment to obtain the superconducting oxide.

4.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the alkoxide precursors are both very expensive and difficult to obtain. In addition, the solubility of copper alkoxides is very low in organic solvents and yttrium alkoxides are readily hydrolysed even by a trace of water. Despite these difficulties, superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been prepared using alkoxides [157, 179–181]. A simple reaction involving $\text{Y}(\text{OCHMe}_2)_3$, $\text{Ba}(\text{OCHMe}_2)_2$ and $\text{Cu}(\text{NBu}_2)_2$ in THF in an argon atmosphere gives the organometallic precursor [157]. The precursor powder, after removal of the solvent, is sintered at 973 K in flowing argon to obtain tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Following oxygenation at 673 K, the product shows a T_c of 85 K. Superconducting properties have been improved by using *n*-butoxides of Y, Ba and Cu in butanol solvent [179].

Alternatively, methoxyethoxides of yttrium, barium and copper have been used as precursors in methoxyethanol-methylethylketone-toluene solvent mixture to prepare $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [180]. In some of the preparations, $\text{Cu}(\text{NO}_3)_2$ (soluble in ethanol) or copper

acetylacetonate (soluble in toluene) is used along with the alkoxides of yttrium and barium to overcome the problem of low solubility of copper alkoxides [182, 183]. Organometallic precursors involving propionates [153] and neodeconates [184] have also been used for preparing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Modified sol-gel methods which do not involve the metal alkoxide precursors have been employed by many workers. Thus, Nagano and Greenblatt [185] have employed metal nitrates dissolved in ethylene glycol. After refluxing around 353 K under vigorous stirring, a bluish green colloidal gel is obtained. The gel is converted into orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by heating to 1223 K in flowing oxygen. Precipitating all the three ions as hydroxides also results in fine colloidal particles of the starting materials [186–188]. The precipitation is generally carried out by the addition of NH_4OH [186], $\text{N}(\text{CH}_3)_4\text{OH}$ [187] or $\text{Ba}(\text{OH})_2$ [188] to a solution of metal nitrates (pH range 7–8). These hydroxides are decomposed around 1223 K in oxygen to give $\text{YBa}_2\text{Cu}_3\text{O}_7$ showing a T_c of 93 K.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been prepared by the citrate gel process [189–193]. In this method 1 g equivalent of citric acid is added to each gram equivalent of the metal. The pH of the solution is adjusted to around 6 (either by NH_4OH or by ethylenediamine). Evaporation of the solvent (water) around 353 K, results in a viscous dark blue gel. The gel is decomposed and the powder sintered in the form of pellets at 1173 K in oxygen to obtain orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (T_c = 93 K). By this method, ultrafine homogeneous powders (particle size $\sim 0.3 \mu\text{m}$) are obtained. The crucial step in this process is the adjustment of the pH which controls the stoichiometry of the final product. This limitation has been overcome by dispersing the citrate metal ion complexes in a solvent mixture of ethylene glycol and water [194, 195].

Problems such as the formation of BaCO_3 during the calcination step, filtration and contamination of alkali metal ions in the final product are avoided in the sol-gel process. Furthermore, perfect homogeneity is obtained before calcination. The sol-gel process (e.g. citrate process) has the advantage over the other methods in that the gel can be used for making thick and thin superconducting films, fibres etc which have technological importance [179, 185, 186, 196–198].

4.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

The sol-gel method offers a good alternative to the ceramic method for the synthesis of superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$. The following procedure has been used to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ at 1 atm oxygen pressure [199]. Appropriate quantities of $\text{Y}(n-\text{OC}_4\text{H}_9)_3$, $\text{Ba}(s-\text{OC}_4\text{H}_9)_2$ and $\text{Cu}(s-\text{O}i\text{Bu})_2$ in butanol-xylene mixture are refluxed in an argon atmosphere at 343 K for a period of 30 h. The fine powder after the vigorous reaction is freed from the solvent and dried. The powder is heated in the form of pellets at 1033 K in flowing oxygen to obtain superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$.

the 124 cuprate is quite rapid. $\text{Cu}(\text{NO}_3)_2$ has also been used as the source of copper in this procedure [200].

In the modified citrate gel process to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ [201, 202], 1 g equivalent of citric acid is added for each gram equivalent of the metal and the pH of the solution is adjusted to ~ 5.5 by the addition of ethylenediamine. The resulting clear solution is evaporated to yield a viscous purple gel. The decomposed gel is sintered in flowing oxygen for 3–5 days at 1088 K to obtain nearly monophasic $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 66$ K). Kakihana *et al* [203] have reported the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ using a precursor obtained from citrate metal ion complexes uniformly dispersed in a solvent mixture of ethylene glycol and water. This method yields phase-pure $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c \sim 79$ K) and eliminates the need to adjust the pH.

4.4. Bismuth cuprates

There have been very few reports of the preparation of bismuth-based cuprate superconductors by the alkoxy sol-gel method [204]. Some of the difficulties arise because the relevant bismuth/lead alkoxides are not readily available; it is also not easy to get a common organic solvent to dissolve the various metal alkoxides simultaneously. Dhalle *et al* [204] have, however, attempted to synthesize the lead-doped $n = 3$ member (2223) using organometallic precursors involving propionates. The starting materials were taken in the form of nitrates and converted into propionates by the addition of an excess of 100% propyl alcohol. This step was followed by the addition of ammonium hydroxide and ethylene glycol to increase the alkoxy anion concentration, thus in turn increasing the viscosity of the solution. All the solutions were mixed together and dried at 353 K. The resin after calcination at 1123 K in air and sintering at 1118 K gave a mixture of the $n = 3$ and $n = 2$ members.

A simple sol-gel method involving the addition of dilute ammonia to an aqueous solution containing nitrates of Bi, Sr and acetates of Ca, Cu and Pb (until the pH of the solution reached around 5.5) has also been employed to prepare bismuth cuprates [205, 206]. The blue solution after concentrating at around 343 K gives a viscous gel. The gel is decomposed and the powder sintered at around 1128 K in air. The product from this procedure is multiphasic showing a T_c of 104 K. The simplicity of the method and the formation of the $n = 3$ phase in a short time makes it somewhat superior to the conventional ceramic route. The modified citrate gel process has been employed to prepare the $n = 2$ member (2212) in pure form with a T_c of 78 K [193].

4.5. Lead cuprates

The modified citrate gel process has been successfully employed by Mahesh *et al* [207] for the synthesis of lead cuprates of the 2213 or 1212 type. In a typical procedure, a mixture of citric acid and ethylene glycol in

solution of the relevant cations. The clear blue solution is concentrated at 373 K in order to get a viscous gel. The gel after decomposition is heated in the form of pellets in the temperature range of 1073–1173 K either in N_2 containing 1% O_2 or in an oxygen atmosphere. $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$ obtained from this process shows a sharp superconducting transition at 70 K. The 1212 cuprate also shows a sharp transition at 60 K. This process is superior to the ceramic procedure for synthesizing superconducting lead cuprates.

5. Alkali flux method

Strong alkaline media, either in the form of solid carbonate fluxes, molten hydroxides or highly concentrated alkali solutions can be employed for the synthesis of high- T_c cuprate superconductors. The alkali flux method takes advantage of both the moderate temperatures of the molten media (453–673 K) as well as of the acid-base characteristics of molten hydroxides to simultaneously precipitate oxides or oxide precursors such as hydroxides or peroxides of the constituent metals. The method stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere.

Employing fused alkali hydroxides, Ham *et al* [208] have synthesized superconducting $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{K}$ or Na or vacancy) at relatively low temperatures (470–570 K). In this method, stoichiometric quantities of La_2O_3 and CuO are added to a molten mixture containing KOH and NaOH (in an approximately 1:1 ratio) in a Teflon crucible and heated at around 570 K in air for 100 h. The 1:1 mixture of KOH and NaOH melts at 440 K and since the alkali hydroxides generally contain some water, the melt is acidic and can readily dissolve oxides such as La_2O_3 and CuO . The black crystals obtained from the reaction (after washing away the excess hydroxide with water) show a T_c of 35 K. Since the reaction is carried out in alkali hydroxides, incorporation of Na^+ or K^+ ions for La^{3+} in the lattice of La_2CuO_4 cannot be ruled out. It should be noted that superconducting alkali-doped La_2CuO_4 is normally prepared at higher temperatures in sealed gold tubes [209]. Recently, alkaline hypobromite oxidation has been employed to obtain $\text{La}_2\text{CuO}_{4+x}$ with a T_c of 44 K [210].

Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c \sim 88$ K) has also been prepared using the fused eutectic of sodium and potassium hydroxides in a similar manner to that described above [211]. The problem of contamination of alkali metals in the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been overcome by using the $\text{Ba}(\text{OH})_2$ flux [211]. The procedure involves heating a mixture containing stoichiometric amounts of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in an open ceramic crucible at around 1023 K in air for a short time (about 10 min) and then slowly cooling the melt to room temperature. Since $\text{Ba}(\text{OH})_2$ has two hydration states, one melting at 351 K and the other at 681 K, the lower-melting hydrate acts as the solvent for the nitrates of copper

and yttrium while the high-melting hydrate serves as the medium for intimate mixing of the reactants. The precipitate obtained from the melt, after washing with water, is sintered in air at around 1173 K followed by oxygenation at 773 K. This method yields an orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase (with little CuO impurity) showing a T_c of 92 K.

The flux method eliminates the need for mechanical grinding and introduction of carbon-containing anions, which is often encountered in the solution routes. Furthermore, the method is efficient and cost-effective.

6. Combustion method

Although many of the solution routes discussed earlier yield homogeneous products, the processes involved are quite complex. Combustion synthesis or self-propagating high-temperature synthesis (SHS), first developed by Merzhanov and Borovinskaya [212], provides a simple and rapid means of preparing inorganic materials, many of which are technologically important. Combustion synthesis is based on the principle that the heat energy liberated by many exothermic non-catalytic solid-solid or solid-gas reactions can self-propagate throughout the sample at a certain rate. This process can therefore occur in a narrow zone which separates the starting substances and reaction products.

Self-propagating combustion has been employed recently in this laboratory to synthesize members of almost all families of cuprate superconductors (except for the thallium cuprates) [213]. The method involves the addition of an appropriate fuel to a solution containing the metal nitrates in the proper stoichiometry. The ratio of the metal nitrates to the fuel is such that when the solution is dried at around 423 K, the solid residue undergoes flash combustion, giving an ash containing the mixture of oxides in the form of very fine particles (particle size 0.3–0.5 μm). The ash is then given proper heat treatment under the desired atmosphere to obtain the cuprate. The small particle size of the ash facilitates the reaction between the metal oxides due to smaller diffusion distances between the cations. Fuels such as urea [213, 214], glycine [213, 215] and tetraformal triazine (TFTA) [216] are generally employed for synthesizing cuprate superconductors. Ultrafine particles of copper metal can also act as an internal fuel wherein the combustion is initiated by flashing a laser beam for a short time [217]. Some of the cuprate superconductors which have been prepared [213] by this route include $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($T_c = 35$ K), $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 90$ K), $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 80$ K), $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ ($T_c = 85$ K), $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$ ($T_c = 60$ K) and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ($T_c \sim 30$ K).

7. Other methods

In addition to the various synthetic methods discussed hitherto, a few other methods such as spray drying [218–221], freeze drying [186, 222, 223], use of metallic precursors [224, 225] and electrochemical methods

[226, 227] have also been employed for the preparation of cuprate superconductors in bulk form. In spray drying, a solution containing the metallic constituents, usually in the form of nitrates, is sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously, leaving behind an intimate mixture of the reactants which on heating at the desired temperature in a suitable atmosphere yields the cuprate. Some of the superconducting cuprates prepared by this method include $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 91$ K) [218], $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 81$ K) [219] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c = 101$ K) [220, 221]. In freeze drying, the reactants (in a common solvent) are frozen by immersing in liquid nitrogen. The solvent is removed at low pressures to obtain the initial reactants in fine powder form, and these are then processed at an appropriate temperature. For example, $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c = 87$ K) [186], $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c = 79$ K) [222] and $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_7$ ($T_c = 101$ K) [223] have been prepared by this method.

Metallic precursors have been used in the preparation of 123 and 247 cuprates [224, 225]. For example, oxidizing an Er–Ba–Cu alloy around 1170 K gives superconducting $\text{ErBa}_2\text{Cu}_3\text{O}_7$ with a T_c of 87 K [224]. Similarly $\text{Yb}_2\text{Ba}_4\text{Cu}_8\text{O}_{15}$ has been obtained by heating an alloy composition of YbBa_2Cu_3 (with 33 wt% of silver) under 1 atm oxygen at 1173 K [225].

Making use of electrochemical oxidation, $\text{La}_2\text{CuO}_{4+\delta}$ with a T_c of 44 K has been prepared at room temperature, which is otherwise possible only by use of high oxygen pressures [226, 227].

8. Oxygen non-stoichiometry

Oxygen stoichiometry plays a crucial role in determining the superconducting properties of many of the cuprates. Thus, stoichiometric La_2CuO_4 is an insulator, while an oxygen-excess material prepared under high oxygen pressures shows superconductivity with a T_c of 35 K [15]. The same holds for the next member of the homologous family, $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ which is superconducting only when there is an oxygen excess [17]. The excess oxygen donates holes in these two systems. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, oxygen can be easily removed giving rise to tetragonal non-superconducting $\text{YBa}_2\text{Cu}_3\text{O}_6$. The $\text{YBa}_2\text{Cu}_3\text{O}_6$ material can be prepared by heating $\text{YBa}_2\text{Cu}_3\text{O}_7$ in an argon atmosphere at 973 K for extended periods of time [228]. The variation of T_c with oxygen stoichiometry, δ , is well known [229, 230]. When δ reaches 0.5, there is an intergrowth of $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, and at this composition, the material shows a T_c of 45 K. The $\delta = 0.5$ composition is obtained by quenching $\delta \approx 0$ material, heated in a nitrogen atmosphere at 743 K [231]. Similarly, by quenching $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 783 K in air, $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (showing a T_c of ~ 60 K) is prepared [231]. The T_c of 90 K is found only when $\delta \leq 0.2$. $\text{YBa}_2\text{Cu}_3\text{O}_6$ is readily oxidized back to $\text{YBa}_2\text{Cu}_3\text{O}_7$. It may be noted that this oxidation–reduction process in

Table 6. Recommended synthetic methods for selected cuprate superconductors.

Cuprate	T_c (K) (approx.)	Methods of synthesis*
$\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	35	Ceramic*, sol-gel, combustion, coprecipitation
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	60	Ceramic (high O_2 pressure)*
$\text{La}_2\text{CuO}_{4+\delta}$	40	Ceramic (high O_2 pressure)* alkali-flux, hypobromite*
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ^b	90	Ceramic (annealing in O_2)*, sol-gel*, coprecipitation*, combustion
$\text{YBa}_2\text{Cu}_4\text{O}_8$ ^b	80	Ceramic (high O_2 pressure), ceramic (with Na_2O_2)* sol-gel*, coprecipitation*
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	90	Ceramic (air-quench)* sol-gel*, combustion, melt (glass) route*
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	110	Ceramic*, sol-gel, melt route
$\text{TlCaBa}_2\text{Cu}_2\text{O}_{8+\delta}$ ^c	90	Ceramic (sealed Ag/Au tube)*
$\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_{8+\delta}$ ^c	115	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$ ^c	90	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	110	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	125	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_{0.5}\text{Pb}_{0.5}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{Pb}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_3\text{O}_8$	70	Ceramic (low O_2 partial pressure)*, sol-gel* (low O_2 partial pressure)
$\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_{2-y}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	45	Ceramic (flowing O_2)*
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	30	Ceramic (low O_2 partial pressure)*
		Coprecipitation (low O_2 partial pressure)*
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*

* Recommended methods are indicated by asterisks.

^b Other rare-earth compounds of this type are also prepared by similar methods. Oxygen annealing is done below the orthorhombic-tetragonal transition.

^c Sr analogues of these compounds with different substitutions at Ca and Tl sites are prepared by a similar procedure.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is of topochemical character. The other analogous rare-earth 123 cuprates also behave in a similar way with respect to the variation of δ with T_c [232].

While $\text{YBa}_2\text{Cu}_4\text{O}_8$ has high oxygen stability, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-\delta}$ shows a wide range of oxygen stoichiometry ($0 \leq \delta \leq 1$) [233]. The maximum T_c of 90 K is achieved when δ is close to zero, and when δ reaches unity the material shows a T_c of 30 K; there is no structural phase transition accompanying the variation in oxygen stoichiometry. Usually, both yttrium 124 and 247 cuprates and their rare-earth analogues, prepared by the ceramic method under 1 atm oxygen pressure, show δ close to zero.

Bismuth cuprates of the type $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4+\delta}$ are best prepared by quenching the samples in air or by annealing in a nitrogen atmosphere at appropriate temperatures [53, 234]. Heating the samples in an oxygen atmosphere is no good, possibly because the extra oxygen may add on to the Bi–O layers. In the case of the lead-doped $n = 3$ member (2223), preparing the samples under low partial pressures of oxygen is found to increase the volume fraction of the superconducting phase [235, 236]. The $n = 1$ member, $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ shows metallic behaviour when there is excess oxygen [237]. By annealing in a reducing atmosphere (Ar or N_2), the excess oxygen can be removed to induce superconductivity.

Oxygen stoichiometry has a dramatic influence on the superconducting properties of thallium cuprates [94, 108, 109, 238–246]. For example, thallium cuprates of the $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$ family, derivatives of the

$\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$ family and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ often have excess oxygen when prepared in sealed tubes. By annealing these samples in a reducing atmosphere (Ar, dilute H_2 , N_2 or vacuum) at appropriate temperatures, the excess oxygen is removed to induce superconductivity in some cases [108, 109, 238]. Annealing at low oxygen partial pressures or in a reducing atmosphere also increases the T_c of some of the superconducting thallium cuprates to higher values by decreasing the oxygen content [94, 239–246]. These variations are clearly related to the hole concentration where the number of holes decreases by removing excess oxygen, thereby giving the optimal concentration required for maximal T_c [247].

In lead cuprates of the $\text{Pb}_2\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_3\text{O}_{8+\delta}$ (2213) type, increasing the oxygen content of the material by annealing in an oxygen atmosphere oxidizes the Pb^{2+} and Cu^{1+} without affecting the CuO_2 sheets, which governs the superconductivity in this material [248]. Though this system shows a wide range of oxygen stoichiometry (associated with a structural phase transition from orthorhombic to tetragonal symmetry), maximum T_c is observed for any given composition where in δ is close to zero [249]. Samples with $\delta \approx 0$ are therefore prepared by annealing in a nitrogen atmosphere containing little oxygen. The lead 1212 cuprates, on the other hand, are best prepared in a flowing oxygen atmosphere. The samples obtained after the oxygen treatment are often not superconducting since there is an oxygen excess. The samples are quenched in air at around 1073 K in order to achieve superconductivity [250].

Superconducting properties of the electron-doped superconductors, $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-\delta}$, are sensitive to the oxygen content. The as-prepared samples which are semiconducting have oxygen content greater than four. Samples with oxygen content less than four are obtained by annealing in a reducing atmosphere (N_2 , Ar or dilute H_2) at around 1173 K. Maintaining the oxygen stoichiometry at less than four is essential for having an oxidation state of Cu less than 2+ in this material [251].

9. Concluding remarks

In the earlier sections we presented details of the preparative methods for the synthesis of various families of cuprate superconductors. In addition, we also examined the advantages and disadvantages of the different methods. Since more than one method of synthesis has been employed for preparing any given cuprate, it becomes necessary to make the right choice of method in any given situation. In order to assist in making such a choice, we have tabulated in table 6 the important preparative methods employed to synthesize some of the representative cuprates, where the recommended methods are also indicated.

Acknowledgment

The authors thank the various agencies, especially the National Superconductivity Research Board, University Grants Commission and the US National Science Foundation for support of the research related to cuprate superconductors.

References

- [1] Bednorz J G and Müller K A 1986 *Z. Phys.* B 64 189
- [2] Sleight A W 1988 *Science* 242 1519
- [3] Rao C N R (ed) 1991 *Chemistry of High Temperature Superconductors* (Singapore: World Scientific)
- [4] Rao C N R 1991 *Phil. Trans. R. Soc. A* 336 595
- [5] Rao C N R and Gopalakrishnan J 1989 *New Directions in Solid State Chemistry* (Cambridge: Cambridge University Press)
- [6] Rao C N R 1992 *Mater. Sci. Eng.* at press
- [7] Uchida S, Takagi H, Kitazawa K and Tanaka S 1987 *Japan. J. Appl. Phys.* 26 L1
- [8] Cava R J, Vandover R B, Batlogg B and Rietman E A 1987 *Phys. Rev. Lett.* 58 408
- [9] Ganguly P, Mohan Ram R A, Sreedhar K and Rao C N R 1987 *Solid State Commun.* 62 807
- [10] Tarascon J M, Greene L H, Mckinnon W R, Hull G W and Geballe T H 1987 *Science* 235 1373
- [11] Wang H *et al* 1987 *Inorg. Chem.* 26 1474
- [12] Bhat V, Ganguli A K, Nanjundaswamy K S, Mohan Ram R A, Gopalakrishnan J and Rao C N R 1987 *Phase Transitions* 10 87
- [13] Kaplan M L and Hauser J J 1988 *Mater. Res. Bull.* 23 287
- [14] Demazeau G, Trese F, Plante Th F, Chevalier B, Etornneau J, Michel C, Hervieu M, Raveau B, Lejay P, Sulpice A and Tournier T 1988 *Physica C* 153-155 824
- [15] Schriber E, Morosin B, Merriell R M, Heava P F, Venturini E L, Kurak J F, Nigney P J, Baughman R J and Ginley D S 1988 *Physica C* 152 121
- [16] Zhou J, Sinha S and Goodenough J B 1989 *Phys. Rev. B* 39 12331
- [17] Cava R J, Batlogg B, Vandover R B, Krajewski J J, Waszczak J V, Flemming R M, Peck W Jr, Rupp L W Jr, Marsh P, James A C W P and Schneemeyer L F 1990 *Nature* 345 6026
- [18] Kinoshita K, Shibata H and Yamada T 1991 *Physica C* 176 433
- [19] Okai B 1991 *Japan. J. Appl. Phys.* 30 L179
- [20] Cava R J, Batlogg B, Vandover R B, Murphy D W, Sunshine S, Siegrist T, Rameika J P, Rietman E A, Zahurak S and Espinosa G P 1987 *Phys. Rev. Lett.* 58 1676
- [21] Rao C N R, Ganguly P, Raychaudhuri A K, Mohan Ram R A and Sreedhar K 1987 *Nature* 326 856
- [22] Leskela M, Mueller C H, Truman J K and Holloway P H 1988 *Mater. Res. Bull.* 23 1469; Hepp A F and Gaier J R 1988 *Mater. Res. Bull.* 23 693
- [23] Rao C N R 1988 *J. Solid State Chem.* 74 147
- [24] Clarke D R 1987 *Int. J. Mod. Phys. B* 1 170
- [25] Umarji A M and Nanjundaswamy K S 1987 *Pramana-J. Phys.* 29 L611
- [26] Tarascon J M, Mckinnon W R, Greene L H, Hull L W and Vogel E M 1987 *Phys. Rev. B* 36 226
- [27] Alario-Franco M A, Moran-Miguel E, Saez-Puche R, Garcia-Alvarado F, Amador U, Barabona M, Fernandez F, Perez-Frias M T and Vincent J L 1988 *Mater. Res. Bull.* 23 313
- [28] Manthiram A, Lee S J and Goodenough J B 1988 *J. Solid State Chem.* 73 278
- [29] Cava R J, Batlogg B, Flemming R M, Sunshine S A, Ramirez A, Rietman E A, Zahurak S M and Vandover R B 1988 *Phys. Rev. B* 37 5912
- [30] Somasundaram P, Nanjundaswamy K S, Umarji A M and Rao C N R 1988 *Mater. Res. Bull.* 23 1139
- [31] Veal B M, Kwok W K, Umezawa A, Crabtree G W, Jorgensen J D, Downey J W, Nowicki L J, Mitchell A W, Paulikas A P and Sowers C H 1987 *Appl. Phys. Lett.* 51 279
- [32] Tarascon J M, Barboux P, Miceli P F, Greene L H, Hull G W, Eibschutz M and Sunshine S A 1988 *Phys. Rev. B* 37 7458
- [33] Xu Y, Sabatini R L, Moodenbaugh A R, Zhu Y, Shyu S G, Suenaga M, Dennis K W and McCallum R W 1990 *Physica C* 169 205
- [34] Karpinski J, Kalds E, Jilek E, Rusiecki S and Bucher B 1988 *Nature* 336 660
- [35] Cava R J, Krajewski J J, Peck W F Jr, Batlogg B, Rupp L W Jr, Fleming R M, James A C W P and Marsh P 1989 *Nature* 338 328
- [36] Pooke D M, Buckley R G, Presland M R and Tallon J L 1990 *Phys. Rev. B* 41 6616
- [37] Hurng W M, Wu S F and Lee W H 1990 *Solid State Commun.* 76 647
- [38] Rao C N R, Subbanna G N, Nagarajan R, Ganguli A K, Ganapathi L, Vijayaraghavan R, Bhat S V and Raju A R 1990 *J. Solid State Chem.* 88 163
- [39] Jin S, O'Bryan, Gallagher P K, Tiefel T H, Cava R J, Fastnacht R A and Kammlott G W 1990 *Physica C* 165 415
- [40] Adachi S, Adachi H, Setsune K and Wasa K 1991 *Physica C* 175 523
- [41] Buckley R G, Tallon J L, Pooke D M and Presland M R 1990 *Physica C* 165 391
- [42] Buckley R G, Pooke D M, Tallon J L, Presland M R, Flower N E, Staines M P, Johnson H L, Meylan M, Williams G V M and Bowden M 1991 *Physica C* 174 383

- [43] Karpinski J, Kusicki S, Kaldis E, Bucher D and Juck L 1989 *Physica C* 160 449
- [44] Tallon J L and Lusk J 1990 *Physica C* 167 236
- [45] Morris D E, Nickel J H, Wei J Y T, Asmar N G, Scott J S, Scheven U M, Hultgren C T, Markelz A G, Post J E, Heaney P J, Veblen D R and Hazen R M 1989 *Phys. Rev. B* 39 7347
- [46] Miyatake T, Gotoh S, Koshizuka N and Tanaka S 1989 *Nature* 341 41
- [47] Wada T, Sakurai T, Suzuki N, Koriyama S, Yamauchi H and Tanaka S 1990 *Phys. Rev. B* 41 11209
- [48] Morris D E, Marathe A P and Sinha A P B 1990 *Physica C* 169 386
- [49] Bordet P, Chaillout C, Chevanas J, Hoveau J L, Marezio M, Karpinski J and Kaldis E 1988 *Nature* 334 596
- [50] Morris D E, Asmar N G, Wei J Y T, Sid R L, Nickel J H, Scott J S and Post J E 1989 *Physica C* 162-164 955
- [51] Michel C, Hervieu M, Borel M M, Grandin A, Deslandes F, Provost J and Raveau B 1987 *Z. Phys.* B 68 421
- [52] Maeda H, Tanaka Y, Fukutomi M and Asano T 1988 *Japan. J. Appl. Phys.* 27 L209
- [53] Rao C N R, Ganapathi L, Vijayaraghavan R, Ranga Rao G, Kumari Murthy and Mohan Ram R A 1988 *Physica C* 156 827
- [54] Sastry P V P S S, Gopalakrishnan I K, Sequeira A, Rajagopal H, Gangadharan K, Phatak G M and Iyer R M 1988 *Physica C* 156 230
- [55] Sastry P V P S S, Yakhmi J V and Iyer R M 1989 *Physica C* 161 656
- [56] Wang Z, Statt B W, Lee M J G, Bagheri S and Rutter J 1991 *J. Mater. Res.* 6 1160
- [57] Torrance J B, Tokura Y, LaPlaca S J, Huang T C, Savoy R J and Nazzari A I 1988 *Solid State Commun.* 66 703
- [58] Tallon J L, Buckley R G, Presland M R, Gilberd P W, Brown I W M, Bowden M and Goguel R 1989 *Phase Transitions* 19 171
- [59] Garcia-Alvarado F, Moran E, Alario-Franco M A, Gonzalez M A, Vincent J L, Cheetham A K and Chippindale A M 1990 *J. Less Common. Metals* 164-165 643
- [60] Ikeda Y, Ito H, Shimomura S, Oue Y, Inaba K, Hiroi Z and Takano M 1989 *Physica C* 159 93
- [61] Maeda A, Hase M, Tsukada I, Noda K, Takebayashi S and Uchinokura K 1990 *Phys. Rev. B* 41 6418
- [62] Sinclair D C, Irvine J T S and West A R 1992 *J. Mater. Chem.* 2 579
- [63] Agostinelli E, Bohandy J, Green W J, Phillips T E, Kim B F, Adrian F J and Moorjani K 1989 *J. Mater. Res.* 4 1103
- [64] Ganapathi L, Sujata Krishna, Kumari Murthy, Vijayaraghavan R and Rao C N R 1988 *Solid State Commun.* 67 967; Statt B W, Wang Z, Lee M J G, Yakhmi J V, Decamargo P C, Major J F and Rutter J W 1988 *Physica C* 156 251
- [65] Balachandran U, Shi D, Dos Santos D I, Graham S W, Patel M A, Tani B, Vandervoort K, Claus H and Poeppel R B 1988 *Physica C* 156 649
- [66] Green S M, Jiang C, Mei Y, Luo H L and Politis C 1988 *Phys. Rev. B* 38 5016
- [67] Varma K B R, Rao K J and Rao C N R 1989 *Appl. Phys. Lett.* 54 69
- [68] Komatsu T, Sato R, Hirose C, Matusita K and Yamashita T 1988 *Japan. J. Appl. Phys.* 27 L2293
- [69] Pandey D, Mahesh R, Singh A K, Tiwari V S and Kak S K 1991 *Physica C* 184 135
- [70] Bloom I, Frommelt J M, Hash M C, Lanagan M T, Hsu C T and Goretta K C 1991 *Mater. Res. Bull.* 26 1269
- [71] Gruber C S, György E M, Gallagher P K, O'Bryan H M, Johnson B W, Sunshine S, Zahurak S M, Jin S and Sherwood R C 1988 *Phys. Rev. B* 38 757
- [72] Shi F, Rong T S, Zhou S Z, Wu X F, Du J, Shi Z H, Cui C G, Jin R Y, Zhang J L, Ran Q Z and Shi N C 1990 *Phys. Rev. B* 41 6541
- [73] Rao C N R, Mohan Ram R A, Ganapathi L and Vijayaraghavan R 1988 *Pramana-J. Phys.* 30 L495
- [74] Zandbergen H W, Huang Y K, Menken M J V, Li J N, Kadowaki K, Menovsky A A, Van Tendeloo G and Amelinckx S 1988 *Nature* 332 620
- [75] Rao C N R, Vijayaraghavan R, Ganapathi L and Bhat S V 1989 *J. Solid State Chem.* 79 177; Losch S, Budin H, Eibl O, Hartmann M, Rentschler T, Rygula M, Kemmler-Sack S and Heubener R P 1991 *Physica C* 177 271
- [76] Darriet J, Soethout C J P, Chevalier B and Etourneau J E 1989 *Solid State Commun.* 69 1093
- [77] Manivannan V, Gopalakrishnan J and Rao C N R 1991 *Phys. Rev. B* 43 8686
- [78] Rao C N R, Nagarajan R, Vijayaraghavan R, Vasanthacharya N Y, Kulkarni G U, Ranga Rao G, Umarji A M, Somasundaram P, Subbanna G N, Raju A R, Sood A K and Chandrabhas N 1990 *Supercond. Sci. Technol.* 3 242
- [79] Manthiram A and Goodenough J B 1988 *Appl. Phys. Lett.* 53 420
- [80] Xiang X D, McKernan S, Vareka W A, Zettl A, Corkill J L, Barbee T W III and Cohen M L 1990 *Nature* 348 145
- [81] Tokura Y, Arima T, Takagi H, Uchida S, Ishigaki T, Asano H, Beyers R, Nazzari A I, Laccorre P and Torrance J B 1989 *Nature* 342 890
- [82] Remschnig K, Tarascon J M, Ramesh R, Hull G W and Rogl P 1990 *Physica C* 170 284
- [83] Arima T, Tokura Y, Takagi H, Uchida S, Beyers R and Torrance J B 1990 *Physica C* 168 79
- [84] Sequeira A, Rajagopal H, Ganapathi L, Vijayaraghavan R and Rao C N R 1989 *Int. J. Mod. Phys.* 3 445; Lee P, Gao Y, Sheu H S, Petricek V, Restori R, Coppens P, Darovskikh A, Phillips J C, Sleight A W and Subramanian M A 1989 *Science* 244 62
- [85] Cheetham A K, Chippindale A M, Hibble S J and Woodley C J 1989 *Phase Transitions* 19 223
- [86] Sheng Z Z and Hermann A M 1988 *Nature* 332 55, 138
- [87] Shimakawa Y, Kubo Y, Manoko T, Nakabayashi Y and Igarashi H 1988 *Physica C* 156 97
- [88] Torardi C C, Subramanian M A, Gopalakrishnan J, McCarron E M, Calabrese J C, Morrissey K J, Askew T R, Flippens R B, Chowdhry U, Sleight A W and Cox D E 1988 *High Temperature Superconductivity* (ed R M Metzger) (New York: Gordon and Breach) p 117
- [89] Vijayaraghavan R, Rangavittal N, Kulkarni G U, Grantscharova E, Guru Row T N and Rao C N R 1991 *Physica C* 179 183
- [90] Goretta K C, Chen J G, Chen N, Hash M O and Shi D 1990 *Mater. Res. Bull.* 25 791
- [91] Schilling A, Ott H R and Hulliger F 1989 *Physica C* 157 144
- [92] Rao C N R, Ganguli A K and Vijayaraghavan R 1989 *Phys. Rev. B* 40 2505; Ganguli A K, Vijayaraghavan R and Rao C N R 1989 *Phase Transitions* 19 213
- [93] Parkin S S P, Lee V Y, Nazzari A I, Savoy R, Huang T C, Gorman G and Beyers R 1988 *Phys. Rev. B* 38 6531
- [94] Martin C, Maignan A, Provost J, Michel C, Hervieu M, Tournier R and Raveau B 1990 *Physica C* 168 8

- [95] Barry J C, Iqbal Z, Ramakrishna B L, Sharma R, Eckhardt H and Reidinger F 1989 *J. Appl. Phys.* **65** 5207
- [96] Gopalakrishnan I K, Sastry P V P S S, Gangadharan K, Phatak G M, Yakhmi J V and Iyer R M 1988 *Appl. Phys. Lett.* **53** 414
- [97] Li S and Greenblatt M 1989 *Physica C* **157** 365
- [98] Ganguli A K, Nanjundaswamy K S, Subbanna G N, Rajumon M K, Sarma D D and Rao C N R 1988 *Mod. Phys. Lett. B* **2** 1169
- [99] Sleight A W 1991 *Phys. Today* **44** 24
- [100] Parkin S S P, Lee V Y, Engler E M, Nazzari A I, Huang T C, Gorman G, Savoy R and Beyers R 1988 *Phys. Rev. Lett.* **60** 2539
- [101] Vijayaraghavan R, Gopalakrishnan J and Rao C N R 1992 *J. Mater. Chem.* **2** 237
- [102] Suigse R, Herbayashi M, Trerada N, Jo M, Shimomura T and Ihara H 1988 *Japan. J. Appl. Phys.* **27** 1709
- [103] Suigse R, Herbayashi M, Trerada N, Jo M, Shimomura T and Ihara H 1989 *Physica C* **157** 131
- [104] Ganguli A K, Nanjundaswamy K S and Rao C N R 1988 *Physica C* **156** 788
- [105] Subramanian M A, Torardi C C, Gopalakrishnan J, Gai P L, Calabrese J C, Askew T R, Flippen R B and Sleight A W 1988 *Science* **242** 249
- [106] Subramanian M A, Gai P L and Sleight A W 1990 *Mater. Res. Bull.* **25** 101
- [107] Pan M H and Greenblatt M 1991 *Physica C* **176** 80
- [108] Pan M H and Greenblatt M 1991 *Physica C* **184** 235
- [109] Ganguli A K, Manivannan V, Sood A K and Rao C N R 1989 *Appl. Phys. Lett.* **55** 2664
- [110] Manivannan V, Ganguli A K, Subbanna G N and Rao C N R 1990 *Solid State Commun.* **74** 87
- [111] Manako T, Shimakawa Y, Kubo Y, Satoh T and Igarashi H 1989 *Physica C* **158** 143
- [112] Martin C, Bourgault D, Hervieu M, Michel C, Provost J and Raveau B 1989 *Mod. Phys. Lett. B* **3** 993
- [113] Vijayaraghavan R 1992 *PhD Thesis* Indian Institute of Science
- [114] Liu R S, Hervieu M, Michel C, Maignan A, Martin C, Raveau B and Edwards P P 1992 *Physica C* **197** 131
- [115] Torardi C C, Subramanian M A, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flippen R B, Chowdhry U and Sleight A W 1988 *Science* **240** 631
- [116] Cava R J *et al* 1988 *Nature* **336** 211
- [117] Koike Y, Masuzawa M, Noji T, Sunagawa H, Kawabe H, Kobayashi N and Saito Y 1990 *Physica C* **170** 130
- [118] Subramanian M A, Gopalakrishnan J, Torardi C C, Gai P L, Boyes E D, Askew T R, Flippen R B, Farneth W E and Sleight A W 1989 *Physica C* **157** 124
- [119] Kadowaki K, Menken M J V and Moleman A C 1989 *Physica C* **159** 165
- [120] Ramprasad, Soni N C, Adhikary K, Malik S K and Tomy C V 1990 *Solid State Commun.* **76** 667
- [121] Retoux R, Michel C, Hervieu M and Raveau B 1989 *Mod. Phys. Lett. B* **3** 591
- [122] Zandbergen H W, Fu W T, Van Ruitenbeck J M and Amelinckx S 1989 *Physica C* **159** 81
- [123] Adachi S, Setsune K and Wasa K 1990 *Japan. J. Appl. Phys.* **29** L890
- [124] Maeda T, Sakuyama K, Koriyama S, Yamauchi H and Tanaka S 1991 *Phys. Rev. B* **43** 7866
- [125] Rouillon T, Provost J, Hervieu M, Groult D, Michel C and Raveau B 1989 *Physica C* **159** 201
- [126] Rouillon T, Maignan A, Hervieu M, Michel C, Groult D and Raveau B 1990 *Physica C* **171** 7
- [127] Liu R S, Wu S F, Gameson I, Edwards P P, Maignan A, Rouillon T, Groult D and Raveau B 1991 *J. Solid State Chem.* **93** 276
- [128] Mohan Ram R A and Clearfield A 1991 *Chem. Mater.* **3** 313
- [129] Maeda T, Sakuyama K, Koriyama S, Ichinose A, Yamauchi H and Tanaka S 1990 *Physica C* **169** 133
- [130] Tang X X, Morris D E and Sinha A P B 1991 *Phys. Rev. B* **43** 7936
- [131] Liu H B and Morris D E 1991 *Phys. Rev. B* **44** 5369
- [132] Tokura Y, Takagi H and Uchida S 1989 *Nature* **337** 345
- [133] Markert J T and Maple M B 1989 *Solid State Commun.* **70** 145
- [134] Markert J T, Early E A, Bjornholm T, Ghanaty S, Lee B W, Neumier J J, Price R D, Seaman C L and Maple M B 1989 *Physica C* **159** 178
- [135] Lopez-Morales M E, Savoy R J and Grant P M 1990 *J. Mater. Res.* **5** 2041
- [136] James A C W P, Zahurak S M and Murphy D W 1989 *Nature* **338** 240
- [137] Felner I, Yaron U, Yeshurun Y, Yacoby E R and Wolfus Y 1989 *Phys. Rev. B* **40** 11366
- [138] Ayoub N Y, Almasan C C, Early E A, Markert J T, Seaman C L and Maple M B 1990 *Physica C* **170** 211
- [139] Takano M, Azuma M, Hiroi Z, Bando Y and Takeda Y 1991 *Physica C* **176** 441
- [140] Takano M, Hiroi Z, Azuma M and Takeda Y 1992 *Chemistry of High Temperature Superconductors* (ed C N R Rao) (Singapore: World Scientific) p 243
- [141] Smith M G, Manthiram A, Zhou J, Goodenough J B and Markert J T 1991 *Nature* **351** 549
- [142] Azuma M, Hiroi Z, Takano M, Bando Y and Takeda Y 1992 *Nature* **356** 775
- [143] Capone D W, Hinks D G, Jorgensen J D and Zhang Z K 1987 *Appl. Phys. Lett.* **50** 543
- [144] Bednorz J G, Takashige M and Müller K A 1987 *Mater. Res. Bull.* **22** 819
- [145] Jorgensen J D, Schuttler H B, Hinks D G, Capone D W, Zhang K, Brodsky M B and Scalapino D 1987 *Phys. Rev. Lett.* **58** 1024
- [146] Otamiri J C and Anderson A 1990 *J. Mater. Res.* **5** 1388
- [147] Panayappan R M, Guy J T, Binstead R, Toysneau V L and Cooper J C 1988 *Phys. Rev. B* **37** 3727
- [148] McIntyre P C, Cima M J, Man Fai Ng, Chiu R C and Rhine W E 1990 *J. Mater. Res.* **5** 2771
- [149] Manthiram A and Goodenough J B 1987 *Nature* **329** 701
- [150] Wang X Z, Henry M, Livage J and Rosenmann I 1987 *Solid State Commun.* **64** 881
- [151] Clark R J, Harrison L L, Skirius S A and Wallace W J 1990 *Mol. Cryst. Liq. Cryst.* **184** 377
- [152] Vos A, Carleer R, Mullens J, Yperman J, Vanhees J and Van Poucke L C 1991 *Eur. J. Solid State Inorg. Chem.* **28** 657
- [153] Vilminot S, Hadigui S El and Desory A 1988 *Mater. Res. Bull.* **23** 521
- [154] Pramanik P, Biswas S, Singh C, Bhattacharya D, Dey T K, Sen D, Ghatak S K and Chopra K L 1988 *Mater. Res. Bull.* **23** 1693
- [155] Kellner K, Wang X Z, Gritzner G and Bauvale D 1991 *Physica C* **173** 208
- [156] Liu R S, Chang C T and Wu P T 1989 *Inorg. Chem.* **28** 154
- [157] Horowitz H S, McLain S J, Sleight A W, Druliner J D, Gai P L, Van Kavelaar M J, Wagner J L, Biggs B D and Poon S J 1989 *Science* **243** 66
- [158] Kini A M, Geiser U, Kao H C I, Carlson D K, Wang H H, Monaghan M R and Williams J M 1987 *Inorg. Chem.* **26** 1834

- D C 1990 *Mater. Res. Bull.* 25 923
- [160] Ho J S, Liu R S, Chang C T and Edwards P P 1991 *J. Chem. Soc. Chem. Commun.* 664
- [161] Chen W L, Huang Y, Wu M K, Wang M J, Chen D H, Sheen S R and Chang C T 1991 *Physica C* 185-189 483
- [162] Guptasarma P, Palkar V R and Multani M R 1991 *Solid State Commun.* 77 769
- [163] Liu R S, Ho J S, Chang C T and Edwards P P 1991 *J. Solid State Chem.* 92 247
- [164] Das Santos D I, Balachandran U, Guttchow R A and Poeppel R B 1990 *J. Non-Cryst. Solids* 121 441
- [165] Zhang Y, Fang Z, Muhammed M, Rao K V, Skumryev V, Medelihu H and Costa J L 1989 *Physica C* 157 108
- [166] Marbach G, Stotz S, Klee M and Devries J W C 1989 *Physica C* 161 111
- [167] Takano M, Takada J, Oda K, Kitaguchi H, Miura Y, Ikeda Y, Tomi Y and Mazaki H 1988 *Japan. J. Appl. Phys.* 27 L1041
- [168] Chen F H, Hoo K S and Tseng T Y 1990 *J. Mater. Sci.* 25 3338
- [169] Hagberg J, Vusimaki A, Levoska J and Leppavuori S 1989 *Physica C* 160 369
- [170] Gritzner G and Bernhard K 1991 *Physica C* 181 201
- [171] Chiang C, Shie C Y, Huang Y T, Lee W H and Wu P T 1990 *Physica C* 170 383
- [172] Chen D Y, Shie C Y, Sheen S R and Chang C T 1991 *Japan. J. Appl. Phys.* 30 1198
- [173] Shie C Y, Liu R S, Chang C T and Wu P T 1990 *Inorg. Chem.* 29 3117
- [174] Bernhard K, Gritzner G, Wang X Z and Bauerle D 1990 *J. Solid State Chem.* 86 293
- [175] Schrodtt D J et al 1988 *Solid State Commun.* 67 871
- [176] Borik M, Chernikov M, Dubov I, Osiko V, Veselago V, Yakowets Y and Stepankin V 1992 *Supercond. Sci. Technol.* 5 151
- [177] Bernhard K and Gritzner G 1992 *Physica C* 196 259
- [178] Kordas G, Wu K, Brahme U S, Friedmann T A and Ginsberg D M 1987 *Mater. Lett.* 5 417
- [179] Shibata S, Kitagawa T, Okazaki H, Kimura T and Murakami T 1988 *Japan. J. Appl. Phys.* 27 L53
- [180] Kordas G, Moore G A, Jorgensen J D, Rotella F, Hitterman R L, Volin K J and Faber J 1991 *J. Mater. Chem.* 1 175
- [181] Katayama S and Sekine M 1990 *J. Mater. Res.* 5 683
- [182] Murakami H, Yaegashi S, Nishino J, Shiohara Y and Tanaka S 1990 *Japan. J. Appl. Phys.* 29 2715
- [183] Catania P, Hovnanian N, Cot L, Pham Thi M, Kormann R and Ganne J P 1990 *Mater. Res. Bull.* 25 631
- [184] Bowmer T N and Shokoohi F K 1991 *J. Mater. Res.* 6 670
- [185] Nagano M and Greenblatt M 1988 *Solid State Commun.* 67 595
- [186] Barboux P, Tarascon J M, Greene L H, Hull G W and Bagley B G 1988 *J. Appl. Phys.* 63 2725
- [187] Fujiki M, Hikita M and Sukegawa K 1987 *Japan. J. Appl. Phys.* 26 L1159
- [188] Karis T E and Economy J 1991 *J. Mater. Res.* 6 1623
- [189] Chu C T and Dunn B 1987 *J. Am. Ceram. Soc.* 70 C375
- [190] Blank D H A, Kruidhof H K and Flokstra J 1988 *J. Phys. D: Appl. Phys.* 21 226
- [191] Sanjines R, Ravindranathan Thampi K and Kiwi J 1988 *J. Am. Ceram. Soc.* 71 512
- [192] Yang Y M, Out P, Zhao B R, Zhao Y Y, Li L, Ran Q Z and Jin R Y 1989 *J. Appl. Phys.* 66 312
- [193] Liu R S, Wang W N, Chang C T and Wu P T 1989 *Japan. J. Appl. Phys.* 28 L2155
- [194] Lee H K, Kim D and Sucks S I 1989 *J. Appl. Phys.* 65 2563
- and Norling P 1989 *Physica C* 162-164 931
- [196] Katayama S and Sekine M 1991 *J. Mater. Res.* 6 1629; 1991 *J. Mater. Chem.* 1 1031
- [197] Zhang S C, Messing G L, Huebner W and Coleman M M 1990 *J. Mater. Res.* 5 1806
- [198] Sakka S, Kozuka H and Zhuang H 1990 *Mol. Cryst. Liq. Cryst.* 184 359
- [199] Koriyama S, Ikemachi T, Kawano T, Yamauchi H and Tanaka S 1991 *Physica C* 185-189 519
- [200] Murakami H, Yaegashi Y, Nishino J, Shiohara Y and Tanaka S 1990 *Japan. J. Appl. Phys.* 29 L445
- [201] Liu R S, Jones R, Bennett M J and Edwards P P 1990 *Appl. Phys. Lett.* 57 920
- [202] Koyama K, Junod A, Graf T, Triscone G and Muller J 1991 *Physica C* 185-189 461
- [203] Kakihana M, Kall M, Borjesson L, Mazaki H, Yasuoka H, Berastegui P, Eriksson S and Johansson L G 1991 *Physica C* 173 377
- [204] Dhalle M, Van Haesendonck C, Bruynseraede Y, Kwarciak J and Van der Biest O 1990 *J. Less Common Metals* 164-165 663
- [205] Tanaka K, Nozue A and Kamiya K 1990 *J. Mater. Sci.* 25 3551
- [206] Masuda Y, Ogawa R, Kawate Y, Tateishi T and Hara N 1992 *J. Mater. Res.* 7 292
- [207] Mahesh R, Nagarajan R and Rao C N R 1992 *J. Solid State Chem.* 96 2
- [208] Ham W K, Holland G F and Stacy A M 1988 *J. Am. Chem. Soc.* 110 5214
- [209] Subramanian M A, Gopalakrishnan J, Torardi C C, Askew T R, Flippen R B, Sleight A W, Liu J J and Poon J J 1988 *Science* 240 495
- [210] Rudolf P and Schöllhorn R 1992 *JCS Chem. Commun.* 1158
- [211] Coppa N, Nichols D H, Schwegler J W, Crow J E, Myer G H and Salomon R E 1989 *J. Mater. Res.* 4 1307; Coppa N, Kebede A, Schwegler J W, Perez I, Salomon R E, Myer G H and Crow J E 1990 *J. Mater. Res.* 5 2755
- [212] Merzhanov A G and Borovinskaya I P 1972 *Dokl. Acad. Nauk.* 204 366
- [213] Mahesh R, Vikram A Pavate, Om Prakash and Rao C N R 1992 *Supercond. Sci. Technol.* 5 174
- [214] Varma H, Warriar K G and Damodaran A D 1990 *J. Am. Ceram. Soc.* 73 3103
- [215] Pederson L R, Maupin G D, Weber W J, McReady D J and Stephens R W 1991 *Mater. Lett.* 10 437
- [216] Sundar Manoharan S, Prasad V, Subramanyam S V and Patil K C 1992 *Physica C* 190 225
- [217] Lepart J P and Varma A 1991 *Physica C* 184 220
- [218] Kourtakis K, Robbins M and Gallagher P K 1989 *J. Solid State Chem.* 82 290
- [219] Kourtakis K, Robbins M, Gallagher P K and Tiefel T 1989 *J. Mater. Res.* 4 1289
- [220] Tomizawa T, Matsunaga H, Fujishiro M and Kakegawa H 1990 *J. Solid State Chem.* 89 212
- [221] Tripathi R B and Johnson D W Jr 1991 *J. Am. Ceram. Soc.* 74 247
- [222] Horn J, Borner H, Semmelhack H C, Lippold B, Hermann J, Wurlitz M, Krotzsch M, Boehnke U, Schlenkrich F and Frenzel Ch 1991 *Solid State Commun.* 79 483
- [223] Song K H, Liu H K, Dou S and Sorrell C C 1990 *J. Am. Ceram. Soc.* 73 1771
- [224] Matsuzaki K, Inoue A, Kimura H, Aoki K and Masumoto T 1987 *Japan. J. Appl. Phys.* 26 L1310
- [225] Kogure T, Kontra R, Yurek G J and Vander Sande J B 1988 *Physica C* 156 45
- [226] Grenier J C, Wattiaux A, Lagueyte N, Park J C, Marquestaut E, Etourneau J and Pouchard M 1991 *Physica C* 173 139

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ FADED TEXT OR DRAWING

☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.